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# A STUDY OF THE WEATHERING OF VOLCANIC TUFFS IN A TROPICAL ENVIRONMENT, INCLUDING THE EVALUATION OF A CONSOLIDANT

Maria Cristina P. Paterno

A THESIS

In

Historic Preservation

Presented to the Faculties of the University of Pennsylvania in
Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

1999

Advisor
Dr. A. Elena Charola
Lecturer in Historic Preservation

Reader
Dr. Gomaa Omar
Lecturer in Earth and
Environmental Science

Graduate Group Chair
Frank G. Matero
Associate Professor of Architecture

Fine Arts

UNIVERSITY
OF
PENNSYLVANIA

## *Acknowledgements*

*To Mom and Dad who never disputed my career shift,*
*and instead supported me throughout;*
*Dr. Charola for her guidance, efficiency and great patience,*
*and to Omar for his tenacious concern for my tutelage.*

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# INTRODUCTION

Studies on the conservation of volcanic tuffs have been prompted by the deterioration of world-renowned monuments such as the rock-hewn churches in the Göreme Valley, Turkey, the statues in Easter Island, Chile, the Cuaucalli Temple, Mexico, and the Angono Petroglyphs, Philippines. Published research on the weathering and preservation of this stone has been relatively recent and sparse when compared with research on other stones: reports of studies of igneous rocks presented in stone conservation congresses totals only 8%[1]. This figure includes studies on granite and basalt; the number of studies on volcanic tuff is fewer still. Of these studies, the bulk focuses on deterioration mechanisms in temperate climates, while significantly fewer studies were carried out for tropical climates.

In general, the study of tropical weathering is a weak area in conservation, for the field itself is a product of European thought which evolved in an effort to save cultural monuments concentrated largely in temperate climates. However, a slowly growing emphasis is being placed on studies of the tropics, which occupies approximately forty percent of the earth's land surface, and is home to nearly half of the world's population. Ninety percent of this area is characterized by a constantly hot and humid climate,[2] a significant departure from the temperate regions' extreme seasonal and diurnal climatic swings.

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[1] C.A. Grissom, "The Deterioration and Treatment of Volcanic Stone: A Review of the Literature" in *Lavas and Volcanic Tuffs,* eds. A.E. Charola, R.J. Koestler, and G. Lombardi (Rome: ICCROM, 1994) p. 8.
[2] Mary Alice Baish, "Special Problems of Preservation in the Tropics" in *Conservation Administration News, Issue 31.* 1987, p. 4.

This thesis brings together two areas in conservation which have been little explored: volcanic tuffs and weathering in a tropical environment. Because most of what is currently known about the weathering of tuffs has been examined from the context of a temperate climate, it may not necessarily apply to the stone's deterioration in the tropics.

Climates strongly influence or even determine the nature of the mechanism by which a stone will weather. Thus the effects of weathering are distinctly different between tropical and temperate climates. In the tropics, seasonal and diurnal temperatures are more constant, and humidity is consistently high. Moreover, annual precipitation from rainfall is almost double the level of precipitation in temperate regions. These differences imply a lower susceptibility to thermal stresses, but more importantly, greater susceptibility to water and moisture. An abundance of the latter then affects other mechanisms which rely on a constant supply of moisture in order to exist, such as biological growth and salt deterioration. Furthermore, it has been shown that of all the mechanisms that facilitate the rate of breakdown of silicates, (which is the main constitutent of volcanic tuffs) the most important is the quantity of water that leaches through the stone.[3]

The disparity in weathering between climates may be further emphasized because of the high porosity of this stone. The large volume of open pores (porosity can vary from zero to over fifty percent,[4] although it mostly falls within the higher end of this range) implies a larger surface area accessible to deterioration factors, thus increasing its

[3] F.C. Loughnan. *Chemical Weathering of Silicante Minerals.* (New York: American Elsevier Publishing company, Inc., 1969.) p. 49.
[4] Allen Lappin. *Preliminary Thermal Expansion Data Screening for Tuffs.* Unlimited Release, p. 4.

propensity to weather as compared to less porous stones. Also, tuff types may vary significantly with location, as for example the red Otowi Tuff of Bandelier National Monument, the yellowish Easter Island Tuff, or the brown flows of the Angono Petroglyphs, Philippines, further diversifying the weathering.

Studies have shown that moisture and water, even without acids or salts, contribute significantly to volcanic tuff deterioration. Investigations on the weathering mechanisms of the tuffs from Easter Island (Charola 1994), (Wendler, Charola, and Fitzner, 1996); the Campania area, Italy (Cinquegrana, Andria and Piccioli, 1996); Cochasqui, Ecuador (Rossi-Manaresi and Chiari, 1980); Aswan, Sinai and the Eastern Desert, Egypt (Helmi, 1994); Malinalco, Mexico (Torres Montes, Alvarez Gasca et al, 1994); and Göreme, Turkey, (Caner-Saltik, Demirci, et al., 1995) conclude that water both dissolved the vitreous matrix of tuffs, and stressed the stone through wet – dry cycles.

The implications for the weathering of this water-sensitive stone in the tropics suggests an accelerated rate of decay due to the availability of water, compounded by other mechanisms directly related with water supply to the stone. Indeed, the disparity in weathering for volcanic tuffs between tropical and temperate climates could be significant.

This poses a challenge for the study of the weathering of tuffs in tropical environments. Research in this area will be particularly valuable to tropical countries that have historically used tuff as one of their primary building materials. One such country is the Philippines, where tuff was widely used during the Spanish colonial period (1565-1898). It is during this period that the oldest monumental architecture was

built, which today comprises the bulk of extant historical buildings. Only over a hundred years old, these edifices are exhibiting various forms of deterioration, yet few structures have received the benefit of study to arrest or slow down the rate of decay.

The aim of this thesis is to correlate high exposure to water and moisture, which is the main deterioration factor in the tropics with the weathering it produces in tuffs. This will be done through comparison of two geologically similar tuffs from the Philippines, locally known as Guadalupe Tuff, which were weathered artificially and naturally. The latter specimens are from the Angono Petroglyphs, a tuff formation over 10,000 years old,[5] whose condition has been assessed for the purpose of conservation. The deterioration mechanism estimated to be mainly responsible for most of the damage to the carvings is the percolation of water and exposure to large amounts moisture.[6] This hypothesis shall be tested by artificially weathering freshly quarried Guadalupe Tuff under similar mechanisms as those postulated to have most damaged the petroglyphs: wet, dry, and high humidity cycles.

The effect of aging on tuffs is measured by subjecting the freshly quarried samples to the same tests and analyses before and after weathering. Any change in the stone is then compared with the weathering observed in the petroglyph specimens. Similarities between the two suggest that the same water-induced mechanism produced the deterioration observed in both the laboratory weathered tuffs and the Angono petroglyphs.

[5] Elmer B. Billedo. *Geology of the Angong Petroglyphs.* Unpublished Report.
[6] A. Elena Charola. *Angono Petroglyphs, Stone Deterioration and Conservation Measures.* Unpublished Report to the National Musuem, Manila, 1988.

To obtain preliminary information for appropriate conservation treatments, a consolidant, Conservare OH Stone Strengthener, was tested on this stone. Treated stones were weathered and analyzed following the same conditions and test methods as those used for untreated samples. The treatment is assessed according to its ability to deter or delay the conditions that resulted from weathering in untreated samples.

An ethyl silicate was chosen as the consolidant because it has shown positive long-term results on the statues from Easter Island, whose deteriorated conditions have been attributed primarily to water due to the local climate (Wendler, Charola, and Fitzner, 1996); (De Witte, et al., 1988).

# CHAPTER 1
# PHILIPPINE TUFFS

## 1.1 BUILDING TRADITION

The tradition of building with stone is a Spanish introduction to Philippine culture. Prior to the Spanish colonization in 1565, indigenous Filipino architecture comprised of wood and thatch. The Spanish adopted the local architecture to build their settlements since this technology was quicker, cheaper, better suited to local climate and terrain, and expedited colonization. Wood and thatch settlements grew to towns, until a fire in 1583 set the whole town of Manila ablaze and ended the proliferation of these building materials. This incident gave rise to a decree four years later to build solely in stone.

The new stone architecture, for the most part a literal translation of Plateresque structures in New Spain, soon evolved to adapt to earthquakes, humidity, and strong sunlight, while at the same time integrating local stylistic tastes. The evolution resulted in a new architectural style, which consisted of a marriage of wood and stone, a fusion of building which reconciled climate and topography. This new style is called Spanish Colonial architecture, arguably the most celebrated historical architectural form in the Philippines.

Colonial houses, termed *bahay na bato* (house of stone), have wooden poles as their main structural members. In the first story, this is sheathed by a stone curtain wall,

while the second story is all wood. This assembly adds pliancy to the structural system, a necessary attribute in an area so frequently hit by earthquakes. Many churches are also constructed with wooden poles, although the curtain wall often continues beyond the ground story. For the same reasons, churches are rarely built very high, and are often squat.

Volcanic tuff, brick, and coral stone were the most commonly used masonry materials. The choice of material depended on its abundance in the area, as well as availability of the required building technology. Tuff was most popular in Manila and its surrounding provinces of Rizal, Tarlac and Batangas. The stones from these quarries were reputedly inferior to those from Meycauayan, Bulacan, whose tuff was stronger and absorbed less water[7].

The introduction of tuff as a building stone is credited to Fray Domingo de Salazar, the first Bishop of Manila, who searched Manila's river banks for a reliable building material. The stone is locally known as *adobe*, perhaps an adaptation of the Arabic term for sun-dried clay, because the stone is soft and easily worked when freshly quarried, and then soon toughens as it weathers.

Most of the monuments built during the Spanish Colonial period were sheathed in stucco. The plaster was not only ornamental, but also practical. Aside from imitating more costly building materials such as sandstones or marble, or serving to unify an otherwise heterogeneous façade of rubble work and cut stone into a refined whole, the

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[7] Fernando Zialcita and Martin Tinio. *Philippine Ancestral Houses.* (Quezon City: GCF Books, 1996.) p.17.

stucco protected the more porous building materials such as tuff and coral stone from the elements. An architectural fad in the mid-1970's which advocated the look of the California missions promoted the removal of plaster in many buildings. Today, some facades have been re-plastered, while others are still left with the stone exposed to the elements. As a result, the tuff stone is deteriorating at a faster pace than it would have, had its protective sheath been left on.

At present, the use of volcanic tuff as a building material is limited to cladding. The stone's inherent brittleness, friability, and heterogeneity make its mechanical properties questionable by today's standards, as it is only a reliable structural material when used in large blocks, as was the case historically.

## 1.2 ANGONO PETROGLYPHS

The Angono Petroglyphs are located on a hill 163 meters above sea level, in the lakeshore town of Angono, Rizal, along the east coast of the Morong Peninsula. The petroglyphs contain 127 figures resembling man, frog and lizard carved into the back wall of a shallow cave that spans 63 meters wide, 5 meters tall, and 8 meters deep (Fig. 1). The carvings are confined to one horizontal wall measuring 25 meters by three meters, with approximately 70% of carvings distributed about mid-height.

The cave developed from a fault which exposed two layers of rock: the upper volcanic tuff layer on which the petroglyphs are carved, and a lower layer of fine grained volcanic ash which has eroded about a foot. Protected by a natural wide stone overhang and a forested ridge, (Fig. 2) the site is secluded and almost indistinguishable from the natural landscape.

Fig. 1 Carvings on main panel, Angono Petroglyph

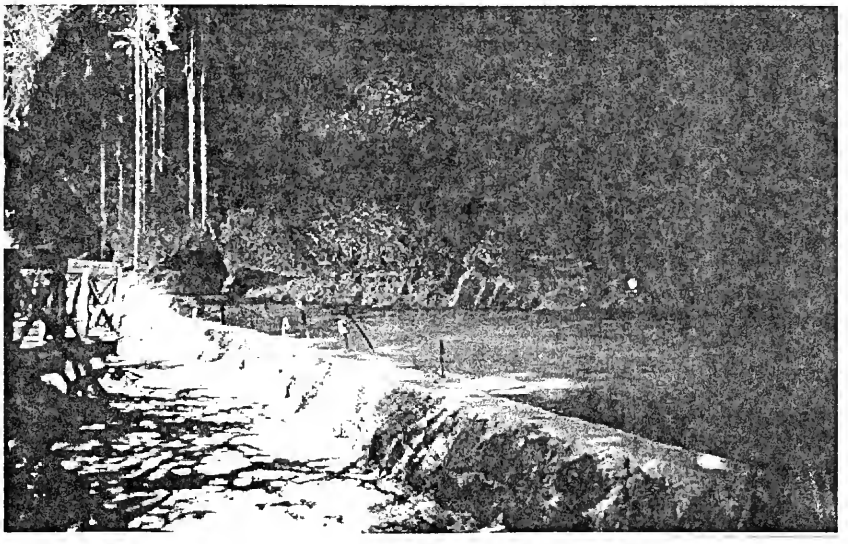

Fig. 2 View of South side, Angono Petroglyphs

Its recent discovery 34 years ago, by the National Artist painter Carlos Francisco, prompted an archaeological investigation by the National Museum. Fragments of obsidian and pottery were unearthed, suggesting the rock shelter was inhabited during the period prior to the introduction of metals to the archipelago. This would date the carvings to the Neolithic Age, around 1,000 B.C. [8]

Cultural significance of the petroglyphs was nationally recognized in 1973 through Ferdinand Marcos' Presidential Decree No. 260, which declared the site a "National Cultural Treasure." However, the cultural pronouncement, as with all succeeding cultural declarations, included no concrete legislation for incentives or penalties designed to protect the site. The area surrounding the petroglyphs is currently being bulldozed and blasted as land is being developed into a golf club, although the site itself has been respected by its owners and developers, Antipolo Properties, Inc. The petroglyph site was donated to the government in 1996, and is currently managed by the National Museum.

The National Museum, entrusted with the management of pre-historic cultural property, began stewardship upon discovery of the site in 1965. The Museum had the vegetation covering the shelter partially cleared, and had moldings of carvings taken. In the early to mid-80's, guards were appointed for day to day management, a drainage trench was constructed in front of the site, and the wall containing most of the carvings was cleaned. Biocides are said to have been applied. Unfortunately, neither the chemical nature nor method of application of cleanser, biocide, and moldings are

[8] Randy Urlanda, "Angono Petroglyphs, Art Exhibit Circa 1,000 B.C.," *Philippine Panorama,* vol. 27 No. 30, (Manila: Manila Bulletin, 1998), p. 5-6.

known. No documents which analyze the nature of deterioration that prompted the treatments, nor pre and post-act photographs can be found. The Museum's last project was the construction of a tunnel entrance under the ridge of the site in 1996 as part of the site development plan.

The cultural significance of the Angono Petroglyphs in world heritage has been acknowledged by the International Council on Monuments and Sites (ICOMOS), listing it in the "World Inventory of Rock Art", and the World Monuments Fund listed it as one of the world's "100 most endangered sites," for which it has received financial assistance for preservation. International consultants such as Dr. Nicholas Stanley-Price and Dr. A. Elena Charola were commissioned to provide technical advice to the National Museum and the Department of Tourism which are jointly undertaking the project.

### 1.2.2 CONDITIONS ASSESSMENT

The site is part of a natural landscape, and as such, includes many forms of vegetation and animal life which can only thrive in an environment that has a constant supply of moisture. Water is suspected to be the main deterioration factor, causing powdering, spalling, and flaking of the petroglyphs. These conditions are most prevalent in areas close to the edges of the overhang, and are presumably responsible for the loss of stone surface. Biological growth and animal infestation pose a lesser threat to the preservation of the petroglyphs, as they are localized. The extent of damage wrought by past interventions on the stone, such as biocidal treatments and molding casts is

difficult to evaluate, for no documentation on substances used nor method of application has been found.

The deleterious effects of capillary rise is evidenced at the base of the site. (Fig. 3). The zone of rising damp exhibits disaggregation and powdering of the surface and softening of the subsurface.

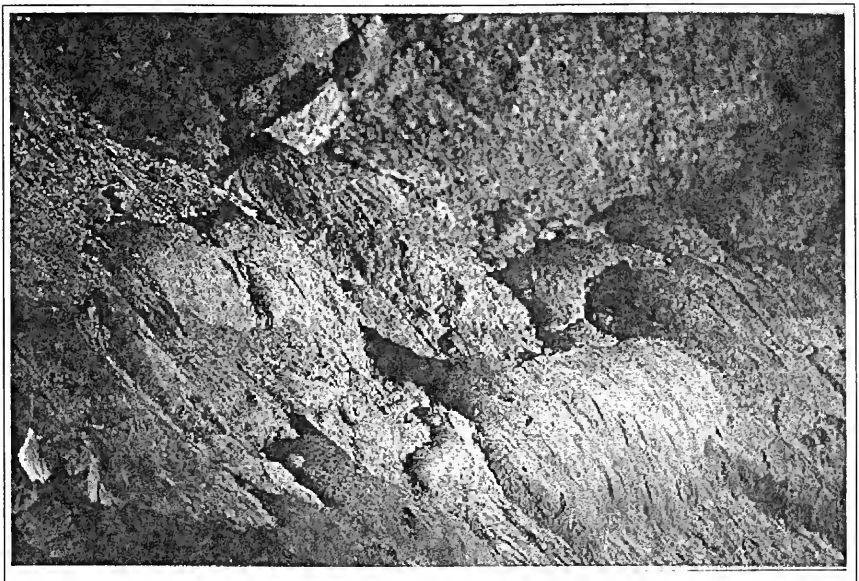

**Fig. 3 Disaggregation due to rising damp at the southern end of panel**

Immediately above this zone, the surface is hardened and suffers from flaking, delamination and spalling. (Fig. 4) It is postulated that the mechanism causing these conditions is water percolating through the hill: the water solubilizes the silica in the matrix and rock fragments, transporting the dissolved silica towards the surface of the

stone. There it evaporates to form a precipitate of amorphous silica which will subsequently harden into the deposit. This reduces the surface porosity of the tuff further impeding the evaporation of water, so that any further silica deposition now occurs at subsurface level. This in turn leads to spalling. The cycle repeats itself as long as there is a sufficient supply of water and moisture to dissolve the silica.[9] White deposits over the hardened surface are prevalent along the main panel and are suspected to be the amorphous silica precipitate. In uncovered areas beyond the span of the overhang, conditions of spalling and disaggregation are

**Fig. 4 Delamination and spalling of hardened layer, South end.**

[9] A. Elena Charola. *The Angono Petroglyphs, Stone Deterioration and Conservation Measures.* Unpublished Report to the National Museum, Manila, Philippines.

aggravated by exposure to direct rain, which accelerates both the process of dissolution and water evaporation.

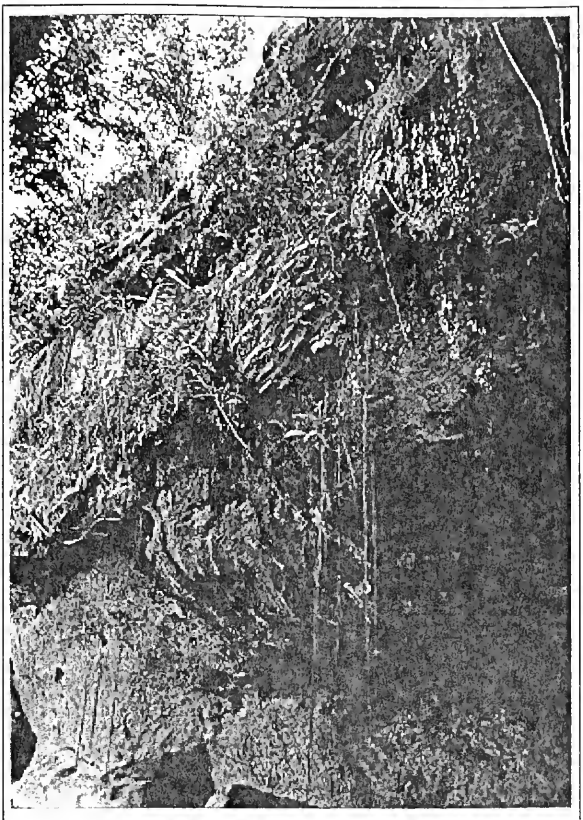

**Fig. 6 Lush vegetation on overhang**

Salts transported by ground water and percolating water are also suspected to exacerbate the above-mentioned conditions by exerting crystallization pressures that lead to disaggregation.

Where moisture is abundant, such as along the overhang and base areas, biological growth is apparent. Root systems hang down from the surface of the overhang (Fig. 6), and algae growth marks the usual course of water flow in this area. Algae also proliferate in continuously damp areas along the wall. Birds nest in open holes, and higher plants have taken root in these damp openings. The relatively few lichen colonizations (Fig. 7) on panels are believed to have appeared only recently, and may be due to the application of a biocide in the mid eighties. Higher plants and burrowing insects appear at the foot of the wall.

Fig. 7 Lichen colonizations in the center panel along the south end

# CHAPTER 2
# THE GEOLOGY OF TUFFS

Tuffs are an igneous rock, a product of solidified magma. Magma is formed by a rise in temperature or drop in pressure within the earth's mantle, which causes its partial melting and displacement, and subsequent expulsion through craters, vents or fissures. The formation of various igneous rock types depends on the elemental composition of the lava, its viscosity, the magnitude of eruption from which it is formed, and the environment in which it cools.

## 2.1 FORMATION

All magmas are similar in elemental composition, but with varying quantities of each: oxygen, silicon, aluminum, iron, calcium, sodium, potassium, magnesium and titanium. Of these, silicon and oxygen comprise 75% of all igneous rocks, forming their dominant minerals, quartz and feldspars. Large amounts of silica in magma generally produces a more viscous melt, while a low silica content increases fluidity. Viscosity or fluidity of the magma has direct influence of the nature of eruption, which, in turn, influences the formation of the rocks. All magmas contain gases which expand under high heat. The expansion of gases causes considerable change in pressure as the melt ascends from the earth's mantle. Because viscous magmas are more able to retain natural gases than magmas with lower viscosities, viscous magmas experience a greater accumulation of pressure, which is released with greater force in an eruption.

During such an eruption, part of the extruded magma is blown to fractions by expansion of gas and sudden contact with water vapor, shattering the lava and sending fragments, droplets, and ash spewing through the air. Rocks formed in this manner are termed pyroclastic rocks and include tuff, scoria and pumice. Whereas scoria and pumice are whole ejections of molten lava that quickly solidified upon cooling (called a pyroclastic flow), tuff is the product of fallen ash over this flow, which has consolidated over time. Tuff contains clasts, (aggregate formed from ejected fragments) which may consist of stones formed during a previous eruption, or newly solidified fragments thrown into the ash deposit. The clasts are cemented together into the stone's matrix as the ash consolidates.

For more fluid magmas, expanding bubbles can shatter the melt, but the pressure is insufficient to blow fragments into air. Instead the fluid mix flows as a *nuées ardentes* or glowing avalanches, which result in welding of the glass fragments together, as was the case for the tuff of the Angono site.

The rate at which the material cools determines the extent of its crystallization. Cooling rates control the time in which ions can move freely to form the crystal structures they are best adapted to. Because volcanic rocks cool above ground, the rate at which they solidify is more rapid, which leaves less time for ions too seek out an orderly crystalline arrangement. Thus they form an amorphous matrix and finer crystals, such as is found in tuffs, obsidian, and pumice.

## 2.2 CLASSIFICATION

Because there are a variety of interrelated factors that determine the nature of igneous rocks, various classifications have likewise been developed. Igneous rocks may be identified according to chemical composition, environment of cooling, grain size and size of clasts. Because a single category does not sufficiently characterize each rock type, rocks are often described using the following categories.

### 2.2.1 CHEMICAL CONSTITUENTS OF LAVA

Generally, rocks with lower silicon content have larger amounts of magnesium and iron, while those with large amounts of silicon have smaller quantities of the said elements. The following classification is based on this premise.

a. *Acidic or Sialic.* These magmas are of low density and high viscosity and contain high amounts of silicon which then crystallize to become free quartz. Acidic rocks contain over 10% free quartz, which imparts its characteristic pale color.

b. *Basic or Mafic.* This magma is denser and of lower viscosity than acidic melts, and contains a lower amount of silicon, which amount is not sufficient to crystallize into free quartz. The rocks are dark in color, due to a higher content of iron and magnesium.

### 2.2.2. ENVIRONMENT OF COOLING

a. *Volcanic*. These are rocks which have formed above the surface, and have cooled rapidly. These rocks are characterized by fine grained or glassy matrices.

b. *Plutonic*. This refers to magmas which have cooled in reservoirs, vents, plugs, and fissures that were conduits for lava on its way to the earth's surface. Having solidified beneath the earth, plutonic rocks have cooled over a longer period. These are generally characterized by larger crystals within the matrix.

### 2.2.3 TEXTURE

For rocks composed of aggregate and matrix, this refers to texture of the matrix.

| | | |
|---|---|---|
| a. | *Glassy* | Amorphous, non-crystalline material |
| b. | *Fine grained* | Presence of crystals undetected with the naked eye but may be seen under the microscope |
| c. | *Coarse grained* | Crystals detectable by naked eye |
| d. | *Pegmatitic* | Containing crystals over 1 cm |
| e. | *Porphyrytic* | Fine-grained or glassy matrix containing coarse crystals |

### 2.2.4 SIZE

This refers to the size of clasts.

| | | |
|---|---|---|
| a. | *Bombs* | Over 65 mm in diameter |
| b. | *Coarse Lapilli* | 65 mm to 32 mm in diameter |
| c. | *Fine Lapilli* | 16 mm to 2 mm |

| | | |
|---|---|---|
| d. | *Coarse Ashes* | 2 mm to 0.25 mm |
| e. | *Fine Ashes* | Less than 0.25 mm |

## 2.3 ANGONO TUFF (PETROGLYPHS)

The petroglyphs site is in the Pleistocene Laguna Formation, of the Quaternary volcanics, formed between 10,000 and 1.65 million years ago. The hill, including the area in which the petroglyphs are carved, is the result of multiple flows consisting predominantly of scoria and pumice, also called Guadalupe tuff. Each flow is distinguished by varying particle sizes and chemical composition, sometimes separated by paleosol horizons, air fall deposits, or pyroclastic surges. Some flows overlap, and are interbedded with pyroclastic surge deposits. Columnar jointings are prominent in these rocks. The topmost layer of the site consists of pyroclastic flow deposits composed of welded to partly welded scoria.[10] The Guadalupe tuff has been characterized as loose and friable, of coarse to fine grain, varying in color from light gray to buff.[11]

## 2.4 MT. MAYAMOT TUFF (QUARRY)

The quarry is part of a quaternary formation, estimated to be of the same origin as that of the Angono site, due to similarities in stratigraphy, composition, formation, and proximity of sites. The rocks are pyroclastic flow deposits of two types, characterized as the following:

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[10] Elmer Billedo. *Geology of the Angono Petroglyphs.* Unpublished report, p. 2.
[11] Silvestre de la Rosa, Jr. *Angono Area, its Geologic Background.* Unpublished Report, National Museum, Manila, p. 8.

a. "Scoria dominated flows; gray to brownish gray; welded to partially welded, or unwelded; locally with columnar jointing; often multiple, overlapping flow units, partially interbedded with pyroclastic surge deposits and air fall units. These deposits constitute generally the upper portion of the pyroclastic flow sequence.

b. Scoria to pumice dominated, multiple flow units; brownish gray, more rarely yellowish cream; dominantly unwelded; individual flow units are distinguishable by different particle sizes and composition; flows may be separated by paleosol horizons, air fall deposits or pyroclstic surge deposits. Individual flow units laterally strongly lenticular."[12]

[12] NIGS/ Philippine German Geology Project. *Geological map of Cardona Quadrangle.* W.U. Scholl, 1989. Sheet 3263 III NE.

# CHAPTER 3
# METHODOLOGY

## 3.1 ANGONO PETROGLYPHS

Samples were obtained for laboratory testing by Dr. Elena Charola during her visit to the Angono petroglyph site in November, 1998. A total of six specimens of deteriorated rock from various weathered areas were studied.

### 3.1.1 TESTS AND ANALYSES

The following tests were conducted on the weathered rock samples, including encrustations and powders proliferating on these.

| SAMPLE | TEST |
|---|---|
| White Encrustations on South Side<br>a. Dry Surface<br>b. Damp Surface | Petrographic Analysis<br>Scanning Electron Microscopy<br>Infra-red Spectrometry |
| Deteriorated Rock Flakes<br>a. South Side<br>b. North Side | Conductance<br>Qualitative Analysis of Soluble Salts<br>Infra-red Spectormetry |
| Powdered Stone Under Indurated Surface, South Side<br>a. 20 cm. above ground<br>b. 1 meter above ground | Conductance<br>Qualitative Analysis of Soluble Salts<br>Infra-red Spectrometry |

### 3.1.2 TEST DESCRIPTIONS

a. ***Petrographic Analyses.*** This analysis enables identification of crystalline minerals, detection of amorphous elements, and an assessment of pore sizes by polarized light mircoscopy of thin sections. A Nikon Optiphot II with polarizing lens was used.

**b.** ***Scanning Electron Microscopy (SEM).*** SEM was used to obtain visual information of surface morphology from a magnification of 100x to 5000x. Due to the extreme porosity of the material, the samples had to be gold sputter coated prior to SEM analysis. To improve observation of this loosely consolidated stone, samples were gold sputter coated.

**c.** ***Infrared Spectrometry (IR).*** This analysis was used to characterize surface deposits which were believed to be amorphous substances which could thus not have been characterized by XRD analysis. A Nicolet 510 P FT-IR Spectrometer was used.

**d.** ***Conductance Measurement / Qualitative Determination of Salts.*** The test serves to check for the presence and concentration of ions in a solution containing a ground sample of material tested. The qualitative identification of ions present helps to identify salt types. Procedures for conductance are based on those specified in NORMAL 13/83, and the qualitative identification of salts are based on the chemical tests described in the Laboratory Manual for Architectural Conservators, 1988, pp. 58-65.

## 3.2 MT. MAYAMOT QUARRY

Fresh rock was obtained from a quarry in Mt. Mayamot, Rizal, Philippines through the quarry's retail site. The specimens' depth from the surface, location and position in the formation are unknown. All samples are taken from two pieces of rock, cut into seven 5x5x5cm cubes, twelve 1x1x1cm cubes, and twelve 1 x 1/2 x 4cm slabs. The quarry was chosen for its geological similarity and proximity to the petroglyph site (both along the east coast of the Morong Peninsula, approximately 25 kilometers apart).

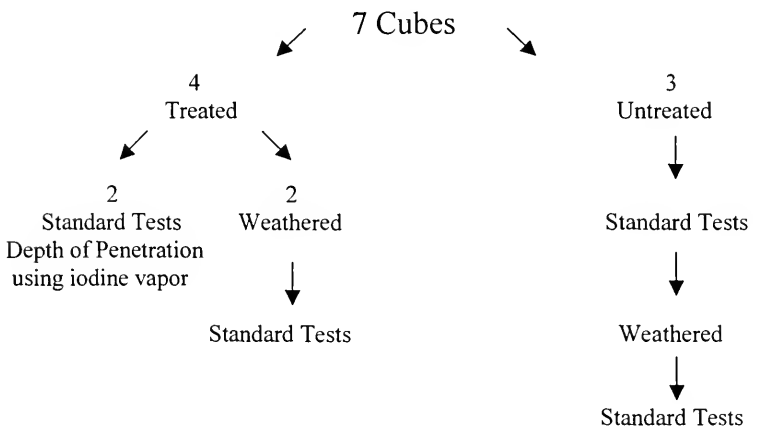
### 3.2.1 TESTS AND ANALYSES

The seven samples were divided into two sets, one set of four cubes was treated with a consolidant and the other set of three cubes was left untreated. Both groups were subjected to the same tests and analyses to determine permeability, mineralogical and chemical composition, morphology and mechanical strength. With the properties recorded, specimens were then artificially weathered. The same tests were repeated on weathered specimens. Test data from both sets were analyzed to determine the nature and extent of weathering. Following is a summary of test methods and their sequence.

### 3.2.2 5X5X5 CUBES

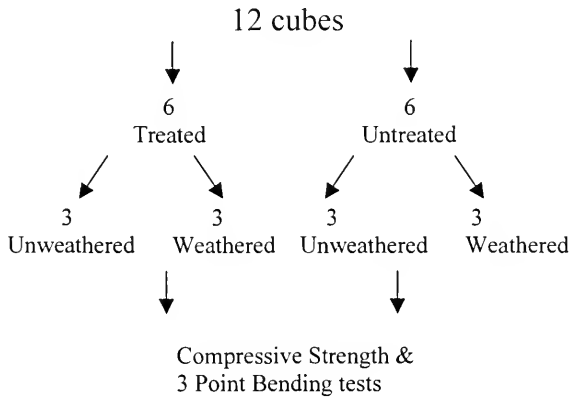
***Standard Tests for Weathered and Unweathered Specimens***

| *Test* | *Source* |
|---|---|
| Capillary Absorption | NORMAL 11/85 |
| Water Absorption by Total Immersion | NORMAL 7/81 |
| Drying Behavior | NORMAL 29/88 |
| Petrographic Analysis | |
| Scanning Electron Microscopy | |
| Infra-red Spectrometry | |



Due to time constraints, the treated samples were divided into two. Unweathered specimens were tested and analysed while the other set was artificially weathered. Thus tests conducted before and after weathering were not performed on the same stones, as was the case in the untreated samples

**3.2.3** **1x1x1 cubes** For compressive strength tests **1x1/2x4 rectangles** For modulus of elasticity




### 3.2.4 TEST DESCRIPTION

A. ***Capillary Absorption of Water / Total Immersion by Water***. These tests measure the stone's open porosity, and capacity to take up and retain water. Because 1 gram of water is equal to 1 $cm^3$, the amount of water absorbed is equated to the open pore space. The capillary absorption test measures the amount of water and rate of absorption per unit surface until saturation, while the total immersion test measures the same by contact of all surfaces with water.

The effect of weathering is gauged by a consistent variance in porosity measurements before and after weathering, which signifies alteration of the pore structure.

Total immersion tests began immediately after successive weighings of 24 hour intervals during the capillary action tests registered difference less than of 0.01%. Procedures followed those specified in NORMAL 11/85.

**B.** ***Drying Behavior.*** This test measures the rate at which water and water vapor evaporates. The rate is the resistance encountered by water as it migrates towards the surface, and is dependent on the material's capillary conduction properties. Because this test is just as much a function of porosity and permeability as the absorption tests, variations in drying rates between weathered and unweathered samples likewise indicate a change in pore structure.

This test immediately follows the water absorption by total immersion test, and was begun once successive weighings of 24 hour registered a difference of less than of 0.01%. Procedures followed those specified in NORMAL 29/88.

**C.** ***Compressive Strength.*** This test measures the compressive load under which a material exhibits permanent deformation and failure. Because the load is applied at constant speed, the test also measures elasticity, indicated by the length of time it took to fail relative to the load. An Instron Testing Machine 1125 was calibrated at a cross head speed of 0.02 inches per minute, and the chart speed at 2.0 inches per minute.

**D.** ***3 Point Bending.*** This measures the stone's ability to resist deformation by flexure, which is a combination of the stone's tensile, shear, and compressive

strengths. Elasticity is indicated by maximum displacement under load, or its tolerance to elastic strain prior to permanent deformation. An Instron 8500 Testing Machine was used, calibrated at a speed of 0.005 inches per second.

### 3.2.5 TESTING RATIONALE

Tests were chosen for their ability to measure properties that were expected to change as a result of weathering. By means of petrographic analyses, characteristics such as mineralogical alteration either by dissolution or redeposition are determined. IR is used to characterize loose and friable material that may have been lost in the process of thin section preparation and non-crystalline substances that cannot be identified by XRD. SEM is used to detect morphological alteration at the micron level. These are changes in porosity and permeability through erosion or obstruction of capillaries and pores, and are reflected in capillary absorption, total immersion and drying tests. Mechanical strength is also altered by erosion of the fabric, decreased grain to grain cohesion or bond strength. These are measured by 3-point bending tests respectively. The altered conditions resulting from weathering shall be compared to observations on the petroglyph tuff derived from the same tests.

To assess the efficacy of the consolidant, all the above tests and analyses, except IR, were conducted on treated specimens. SEM is used to determine the efficacy of the treatment's coating properties and distribution throughout the material. Mechanical stress tests assess the change in strength, while water absorption and drying index tests assess any changes in water related properties.

## 3.3 WEATHERING

Specimens were subjected to a total of 21 weathering cycles, each cycle consisting of the following:

- 1 hour immersion in 60°C distilled water, and left to cool to room temperature, about 18°C
- Patted with paper towel and then hot-air dried at about 40°C for 1½ hours, the time required to evaporate approximately 50% of the absorbed water
- 1 hour immersion in 60°C distilled water, and cooled to room temperature, about 18° C
- Towel dried and then hot-air dried at about 40°C for 1½ hours, the time required to evaporate approximately 50% of the absorbed water
- 19 hour exposure to 100% relative humidity

The artificial weathering cycle is an approximation of the mechanism which is often cited as the leading cause of deterioration in tuffs: high exposure to water and water vapor, and drying stresses. The simulated cycle is by no means representative of the full range of typical tropical stresses; however, it is the basis upon which other mechanisms, such as biological growth, and salt crystallization, are closely dependent.

The samples are artificially weathered at roughly double the average temperatures in the Angono Petroglyphs site. Temperature on site ranges approximately from 22°C to 29°C and seasonal relative humidity fluctuates from 65.5% to 85%.[13] It has been shown that evaporation rate increases about five times when exposed to a mild breeze, and about

[13] Data for Quezon City, Metro Manila. This is the closest area to Angono that has recorded climatorlogical data. Source: Climatological Normals of Science Garden, Quezon City, for the period 1961-1995. Philippine Atmospheric, Geophysical, and Astronomic Services Administration.

three times under exposure to sun.[14] Hot air blowers are used to accelerate these occurrences by constant production of a strong breeze and heat (Fig. 8).

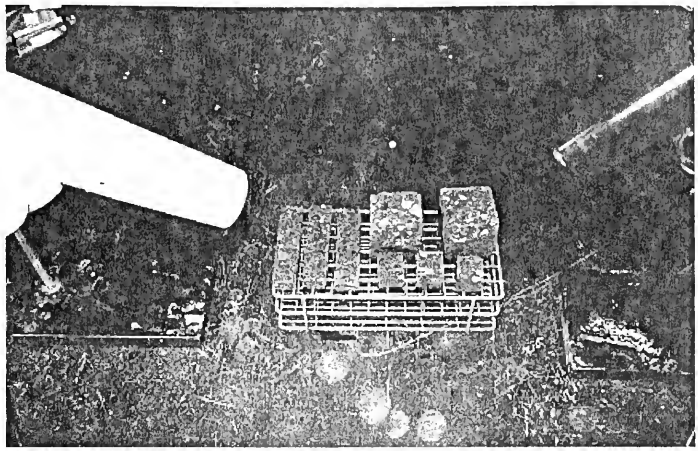


**Figure 8** **Hot air blowers simulating 35°C to 40°C wind**

Total immersion in water and RH exposure of samples was carried out in a closed plastic container. The cycle begins with samples immersed in water preheated to 60°C and allowed to cool to room temperature (about 18°C) while fully immersed. After an hour, samples were removed from the water, wiped with a dry paper towel to absorb excess water, and then dried by hot air dryers for about 1½ hours until approximately half of the absorbed water evaporated. Temperature of the hot air was taken at a distance of about 1 cm from the stones in order to ensure that it ranged within 35°C to 40°C, double the average temperature on site. The water was again preheated to 60°C, the samples returned to the container, and the cycle was repeated a second time. At the end of

[14] Giovanni and Ippolito Massari. *Damp Buildings Old and New.* (Rome: ICCROM, 1993) p. 28.

the last drying cycle, specimens were returned to the container and rested on plastic grids that left the stones above the water level (Fig. 9). The lid of the container was lined with paper towels to absorb vapor and prevent collection of water that would have otherwise

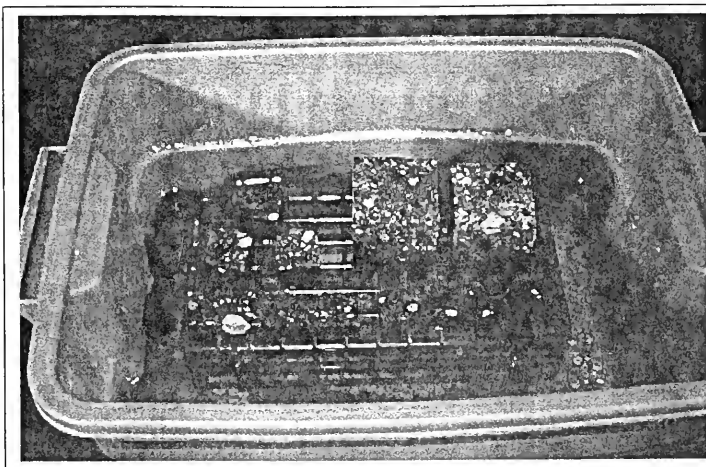


**Figure 9** **Simulated weathering of 100% RH**

dripped onto the specimens. The container was covered to simulate 100% RH, and left for 19 hours. This ended the cycle.

The water in which the stones were weathered was never replaced. Distilled water was added periodically to ensure that the stones were fully immersed.

### 3.4 Rationale for Treatment

Friability, flaking and spalling have been cited as common patterns of deterioration in tuffs. Consolidants, designed to restore or improve cohesion lost by weathering would thus be a rational choice of treatment. Although consolidants are not

weathering would thus be a rational choice of treatment. Although consolidants are not inherently hydrophobic and thus cannot protect the stone from attack by water and moisture, the treatment does strengthen the stone, and consequently slows down the deterioration rate. Furthermore, past studies on the application of consolidants on tuffs report that this treatment is most effective when used without the support of a water repellent. (Lukaszewicz, 1994); (Rossi-Manaresi and Chiari, 1980); (De Witte, et al., 1988).

The criteria used in selecting the product type is in part tailored to the consolidant's applicability and performance in a tropical environment as well as compliance with basic criteria:

a. *Low viscosity.* This is required to enhance penetration into a highly porous material with fine pores.

b. *Minimal reduction of permeability to water vapour.* The treatment must not prevent the passage of water vapor, so that in the event that liquid water enters the stone, it can still evaporate out.

c. *Ability to evenly distribute consolidating material into the stone.* The solvent should not cause migration of the consolidant to the surface upon evaporation.

d. *Low chemical reactivity.* This minimizes potential chemical alteration of the original stone and formation of by-products.

e. *Stability to UV light and oxidation.* Bonds that do not break or are chemically altered by exposure to oxygen or UV.

f. *Applicable under highly humid conditions and sustainability under such environment.* Sufficient polymerization or solidification of consolidant under an RH range that accommodates at least the lowest RH in the Philippines.

g. *Ability to screen against atmospheric pollutants and biological agents.*

h. *With comparable thermal, hygric and mechanical properties to the stone.* Most consolidants will increase the material's tolerance to the above stresses, but this increase should not substantially alter its properties so as to detrimentally affect the stone by inducing more stress in the long run. A consolidant will not always reach all areas of the stone upon application, or may wear away. A large difference in properties between coated and uncoated areas could exacerbate the stress in unprotected areas.

i. *With an effective glass transition temperature that will not flow under 40 C.*[15]

This property indicates the consolidant's softness with regards to temperature. At temperatures above the glass transition point, the consolidant becomes susceptible to cold flow with increasing temperatures, leading to weakening of cohesive bonds and dirt pick-up. At temperatures below this point, the consolidant stiffens, leading to cracking under stress.

[15] Temperature specified for glass transition temperature for semi-permanent coatings. C.V. Horie, *Materials for Conservation.* (London: Butterworth & Co., 1987), p. 78.

l. *Minimal shrinkage upon curing.* Any shrinkage in the consolidant means additional stress in the stone. Less stress from shrinkage is always preferable.

m. *Ease of Use.* This is prescribed by the author in anticipation of use in the Philippines, where large scale application will be executed by contractors and masons with no prior experience with the treatment. The treatment should require minimum preparation, and the conditions and application procedure must be closely followed to maximize the consolidant's long term performance.

n. *Long term ability to sustain above requirements.*

o. *Retreatability.*

### 3.4.1 SELECTION OF CONSOLIDANTS

It is utopian to expect a single product to fulfill the above specifications, for no treatment, nor combination of treatments is known to have been that successful. For example, long term performance is specific to both material and site, and thus has not been proven for any consolidant. The issue of reversibility is possible only in theory, and is irrelevant for the treatment of deteriorated stones. Each product has its own disadvantages; nonetheless, these do have optimal properties which may compensate for their shortcomings in each particular instance. The most prudent choice of treatment would be one whose salient characteristics are optimized for the given problem, environment and material.

The multiplicity of narrow capillaries and extreme porosity of tuffs requires a low

viscosity treatment. By this virtue, waxes, zinc and magnesium flourosilicates are excluded from consideration. The ability to withstand oxidation and harsh UV and high temperatures in a tropical environment is also necessary. Cellulose nitrates and polyethylenes, both subject to photo-oxidation do not comply with this specification. In addition, polyethylenes along with polyvinyl acetates have low glass transition temperatures, which makes them susceptible to flow at lower temperatures. Moreover, the adhesive power of PVAs are lowest on siliceous surfaces, and thus would not adhere well to tuffs. Sodium and potassium silicates are likewise inadvisable for they cause the formation of soluble salts as by-products.

Epoxies and polyesters are comparatively more troublesome to use as they are require two-part systems. The suitability of the mix depends on the accuracy of the mason or contractor, thus adding an extra variable that may complicate the treatment process. This risk is best avoided, for reasons specified in section 3.4, by using one part systems.

By a process of elimination, this leaves the more popular consolidants, silicate esters and acrylic resin solutions. Previous experiments on the consolidation of tuffs show that silica-based products gave good results as it is chemically akin to the siliceous stone.

### 3.4.2 ALKOXYSILANES

Alkoxysilanes are being widely used in stone conservation. Its polymers are based on a silicon-oxygen-silicon backbone with alkoxy groups, allowing eventual cross polymerization by hydrolysis and condensation. Tetraethoxysilane, also known as TEOS,

or tetraethyl silicate is the most commonly used polymer.

This treatment fulfills most of the mentioned criteria for consolidants. Ethyl silicates are chemically akin to siliceous stone (Fig. 10) once it polymerizes, making it a suitable replacement for siliceous binding material. Because the treatment is similar to the tuff's natural cement, it does not substantially alter the stone's original mechanical, thermal and hygric properties.

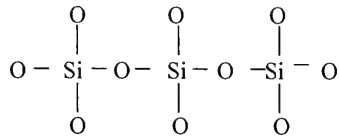


Fig. 10 Partly polymerized ethyl silicate

The low molecular weight of this compound gives it the necessary viscosity for deep penetration into such a porous stone as tuff. In addition, alkoxysilanes are prepolymers in solution which subsequently polymerize after application. Introduction of this prepolymer into the stone allows the smaller molecules to slide past one another more freely than if introduced as a longer polymer. Its viscosity of 0.6 cP at 20°C is lower even than that of water, 1.0 cP at 20°C.[16] Ethyl silicates are highly vapor permeable, thus their application should not significantly alter drying rates nor hygroscopic moisture contents in the stone. Being silicon based, it is also highly resistant to UV degradation and oxidation. It is a one part system of diluent and catalyst, which makes application easier for the inexperienced user.

[16] C.A. Grisson and N.R. Weiss. "Alkoxysilanes in the Conservation of Art and Architecture: 1861-1981," in *Art and Archaeology Technical Abstracts, 18,1* (New York: NP, 1981), pp. 150-201.

Commonly, its rate of shrinkage upon solidification is minimal, and its capability to evenly distribute within pores is satisfactory. However, these properties are both dependent on the degree of polymerization.

Ethyl silicates polymerize by hydrolysis and condensation. When deposited into the stone, the alkoxy groups in the prepolymerized alkoxysilane react with the water from any moisture within the stone. This reaction produces a silanol which then condenses to form a polymeric silica gel. Simultaneous with this reaction is the evaporation of the solvent methyl ethyl ketone and the ethyl alcohol resulting from the hydrolysis. Both are non-reactive to the stone and leaves no by-products. Aside from reducing the viscosity of the solution, the solvent also induces the miscibility of water to the alkoxysilane which facilitates the hydrolysis reaction.

The polymer gel produced by the hydrolysis reaction builds a Si-O-Si network as it condenses, shrinks and hardens around intergranular spaces. This binds particles together, and consolidates and strengthens the stone.

There is a delicate balance between solvent volatility, amount of catalyst, humidity and their effect on rate and degree of polmerization. An insufficient amount of catalyst could allow premature evaporation of the solvent prior to adequate polymerization of the consolidant; on the other hand, too much catalyst could cause rapid polymerization before adequate penetration of the monomer is achieved. The application of silicic esters in conditions of low relative humidity or high wind causes rapid evaporation, which makes it less likely that sufficient hydrolysis and polymerization will occur, resulting in poor consolidation.

### 3.4.3 TREATMENT METHODOLOGY

Samples were treated with Conservare OH Stone Strengthener according to manufacturer's specifications,[17] which were sent with the ordered product. It must be noted that the data sheet was published in 1996, and ProSoCo has since modified some specifications, which include prolonging the minimum curing time from two weeks to three. Modifications did not accompany the old data sheet, and the specifications set in 1996 were followed.

Applications were made in cycles, each cycle consisting of three applications to saturation spaced 10 minutes apart. Cycles were spaced 30 minutes apart to allow adequate penetration. A maximum of three cycles (9 applications) is stipulated; when this limit is reached, the stones must sit for two weeks to allow curing. After this curing period, the second run of three cycles (9 applications) was started. Whereas a typical treatment might involve two to three cycles (6-9 applications) until saturation, the tuffs required a total of six cycles (18 applications) to achieve saturation.

The treatment was applied using a foam brush, using two even strokes per face. Curing was done in a fume hood at room temperature, about 22°C, and an RH of 70%.

[17] ProSoCo Inc., Conservare OH Stone Strengthener Product Data Sheet, (Kansas: ProSoCo, Inc., 1996).

# CHAPTER 4

## CHARACTERIZATION OF ANGONO TUFF SAMPLES

Weathering occurs as a reaction to a change in environment from that in which the minerals were formed. Exposure to water, oxygen, carbon dioxide and other components in the new environment may render a mineral unstable by loosening and destroying its structure and liberating cations into the solution. Chemical alteration by hydrolyisis and hydrogen replacement of cations continues until a state of equilibrium is attained. Dissolved minerals are reconstituted with components from the environment to form secondary products that are comparatively more stable than the initial form.

Of the factors that facilitate the rate of breakdown and generation of secondary products, the most important is the quantity of water leaching through.[17] Thus for regions that experience a high amount of precipitation such as the petroglyph site (2,432 mm. annual rainfall),[18] alteration generally proceeds more readily. The study of weathering of this water-sensitive stone begins with the characterization of the samples from the naturally weathered petroglyph site and continues with that of the artificially weathered quarry specimens.

The strong similarities between the observed conditions of the two sets, naturally and artificially weathered, suggest that the mechanism used for the latter (wet, dry and high humidity cycles) is the same that produced the weathering of stone in the petroglyph site.

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[17] F.C. Loughnan. *Chemical Weathering of Silicate Minerals.* (New York: American Elsevier Publishsing Company, Inc., 1969) p. 49.

[18] Philippine Atmospheric, Geophysical, and Astronomical Servies Administration. *Climatological Normals of Science Garden, Quezon City for the period 1961-1995.*

Salient geological properties of both the freshly quarried and Angono petroglyph samples fall within the same general characteristics as those listed for the stone locally known as Guadalupe tuff. This facilitates the comparison between weathered conditions produced by artificial and natural weathering. That is, geologically similar stones are more likely to generate the similar results than geologically dissimilar stones when subjected to the same stimulus.

## 4.1 PAST STUDIES

Past studies have cited most conditions observed in this stone. Of these, the most common is the condition of disaggregation and spalling, which is often attributed to the dissolution of the vitreous substances, wet-dry stresses, or the action of salts. The formation of white amorphous silica efflorescences has also been cited. However, no condition as the darkened, indurated layer of amorphous silica in the Angono Petroglyphs has been found.

Wendler, Charola and Fitzner (1996), J.P Pauly, J. Loppion and J. Saugnac (1994), and J. Vouvé et al. (1994) cite the presence of a whitish efflorescence identified as an amorphous silica deposited on the surface of some Easter Island statues, where frequent rain events and wind result in repeated wet-dry cycling. The depositions are believed to have been formed by the dissolution of the vitreous matrix by water, which were subsequently re-deposited on the surface. The presence of the silica was not reported to have generated any other conditions or further the deterioration of the stone. Hyvert (1973), Domaslowsky, (1981) and Charola and Lazzarini (1988) agree that

rainfall is the main agent of cracking, flaking, powdering and erosion in the statues, followed by wind erosions, and then salt decay[19].

A study by Bates (1962) of the alteration of glassy constituents in basalt weathered by the tropical climate of Hawaii (rainfall 400 inches per annum signifying rapid decomposition of the glass) shows alteration of the volcanic glass to an amorphous hydrated aluminum silicate.[20]

Salts are rarely attributed to be the main mechanism of the destruction in this stone, and are often cited as merely compounding the deterioration inititated by water. Studies by R. Rossi-Manaresi (1976), R. Rossi-Manaresi and A. Tucci (1994), Wendler, Charola and Fitzner (1996), and J.P Pauly, J. Loppion and J. Saugnac (1994), E.N. Caner-Saltik, et al (1993), L. Lazzarini, et al. (1996), L. Cinquegrana S. Andria and C. Piccioli (1996), and A. Colantuono et al (1993) allude to the secondary role of chlorides in the deterioration of a variety of tuffs. This is not to say, however, that the role of salts should be underestimated, for these can accelerate conditions such as disaggregation, powdering, flaking and spalling that would otherwise have occurred at a slower rate if salts were absent. As previously mentioned, the small pore size distribution and low tensile strength of this stone puts this stone to greater risk of susceptibility to crystallization pressures.

Rossi Manaresi and A. Tucci (1994) theoretically calculated crystallization pressures based on the pore size distribution of two types of fine grained tuff. Total

[19] Lorenzo Lazzarini et al. "New Data on the Characterization and Conservation of the Easter Island's Pyroclastics Used for the Moais" in *Proceedings of the 8th International Congress on Deterioration and Conservation of Stone.* Edited by Josef Riederer. (Berlin: Moller Druck und Verlag Gmbh, 1996), p.1150.

[20] F.C. Loughnan. *Chemical Weathering of Silicate Minerals.* (New York: Americal Elsevier Publishing Company, 1969.) p.81.

pressures exerted by the salt on pores range from 405 to 1258 N/cm$^2$. Although the pore size distribution of the Angono tuff is not known, it is assumed that pore sizes closely approximate the range from the above study, so these are likely to fall prey to a similar range of pressures. The average tensile strength of artificially weathered, untreated tuffs is 290 N/cm2. It can thus be deduced that the petroglyph site tuff which has weathered by multiple mechanisms for over centuries more, is significantly weaker and is thus more likely to be affected by the salts.

Fratini, et al. (1994) cite the occasional generation of kaolinite as a product of de-vitrification of the matrix, while T. Topal and V. Doyuran (1994) and E.N. Caner-Saltik, et al. (1995) cite its presence in small quantities in altered rock fragments. All authors conclude that the presence of these highly expansive clays swell with moisture and can fracture and disaggregate the stone, or leach out the stone and increase porosity. However, the negligible clay content in the Angono tuff and its presence only on the exterior of the petroglyphs relegates cyclical expansion and contraction to a secondary role, as will be shown in the following sections.

## 4.2 ANALYSIS

### 4.2.1 MICROSCOPY

The matrix comprises approximately 70% of the tuff, while the remaining 30% are rock fragments such as pumice, basalt, and scoria. As seen in thin sections, the matrix is unwelded in nature, and is composed of roughly 70% glass and 20% feldspars. Clay content is negligible.

Feldspars range from tiny inclusions of 0.01mm. to approximately 1 mm (Fig.11). The feldspars are visibly weathered, judging by substantial loss of the mineral, poorly defined twinning, and numerous fractures (Fig. 12). These also exhibit yellow staining which is most likely due to leached iron. Viewed under uncrossed polars, the entirety of the sections appears almost invariably a faint yellow-brown. All four cross sections (two thin sections each from the south and north sides) appeared homogeneous with regards to degree of weathering and showed no particular stratigraphy which may indicate depth of alteration.

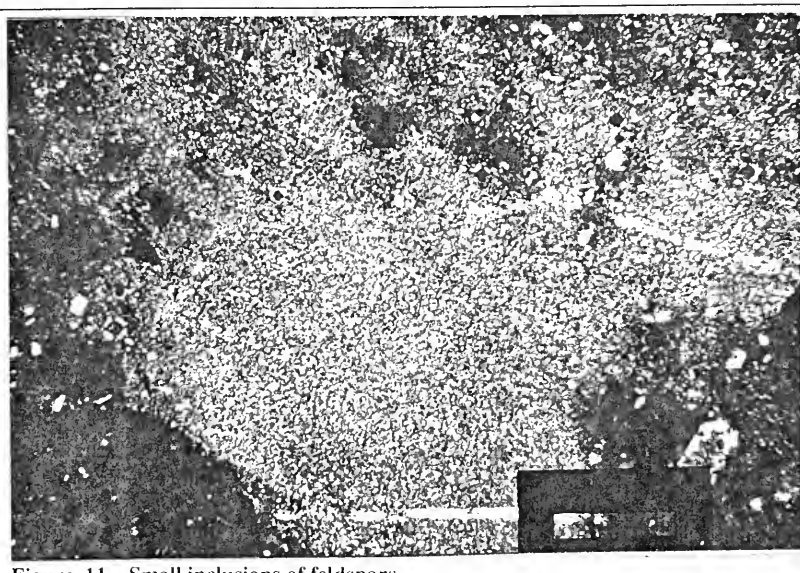

**Figure 11 Small inclusions of feldspars**
**Polarized light micrograph, crossed polars, 25 x magnification**

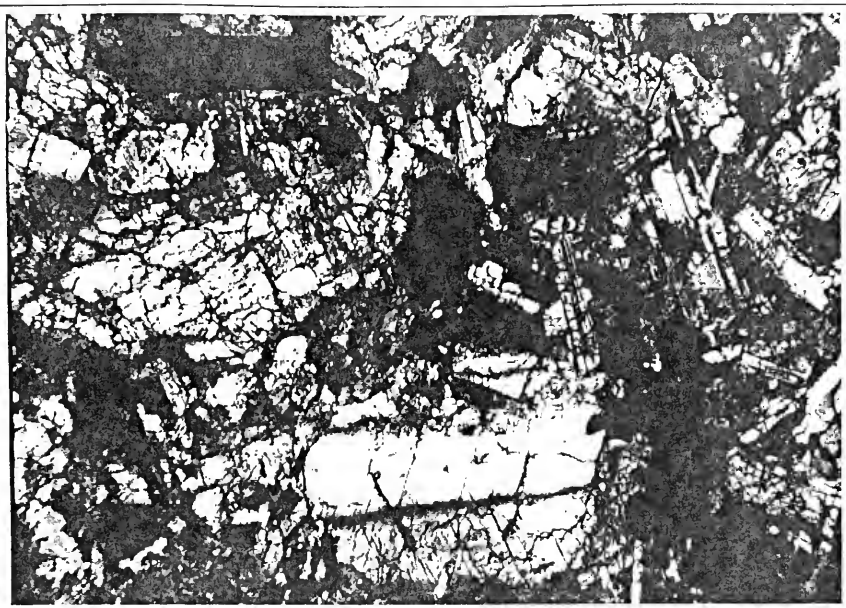

**Figure 12** **Highly fractured feldpsars resulting from weathering Polarized light micrograph, 25 X magnification.**

The homogeneous appearance in thin section may indicate that the stone had weathered to a depth that went beyond the area of the sample. Thus the entire sample was weathered, and did not include sound stone which would have contrasted with deteriorated areas.

Depositions of amorphous silica and zeolites, (aluminosilicates with intense ion-exchange properties), were observed in vacuoles (Figs. 13 and 14). It is uncertain whether these were formed during diagenesis or were a product of the weathering process.

**Fig. 13 Amorphous silica (1) and zeolites (2) in pores**
**SEM Micrograph, x 1,100**

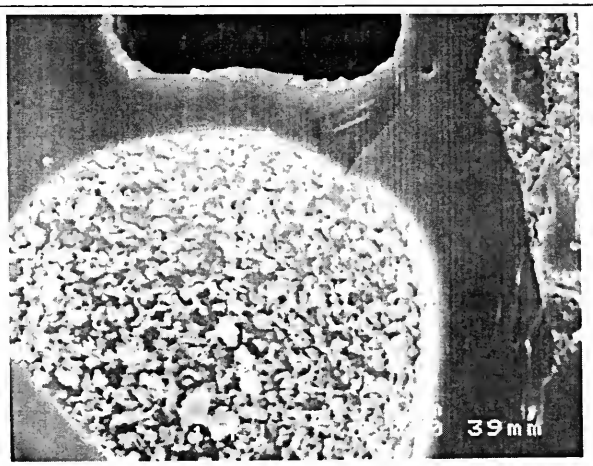


**Fig. 14 Close-up of zeolite in vacuole**
**SEM Micrograph, x 5,000**

### 4.2.3 STRATIGRAPHY

The stone is coated by two deposits of varying thickness (Fig. 15). The topmost layer is a whitish deposit which occurs as a thin stratum, and beneath this is a darkened layer which appears to have been formed by the deposition of a substance that darkened and consolidated the stone (Fig. 16). The upper layer was revealed by SEM to be a soft and light coating (Fig. 17). When mechanically separated from the stone and subjected to IR analysis, the substance was characterized as a mixture of kaolinite and gypsum. Due to the thinness and uneven distribution of this layer, it was not detected in thin section. IR analysis showed the second layer to be an amorphous silica with traces of kaolinite (see IR spectra in appendix). This vitreous layer is denser and less porous than the original stone (Fig. 18 & 19) and could very possibly cause a decrease in original permeability to water and water vapor, thus increasing equilibrium moisture content.

While this stratigraphy is very pronounced in cross section, it is not at all apparent in thin section. This indicates that the deposition contains no crystalline materials which would have been easily detected from the mineral concentration in the layer. Thus detection of this strata is difficult because it is an amorphous silica deposit coating a siliceous stone. Moreover, the visual demarcation of this layer may be evident only when seen in considerable thicknesses, such as in cross section, and less apparent in thin section because color concentration is diminished.

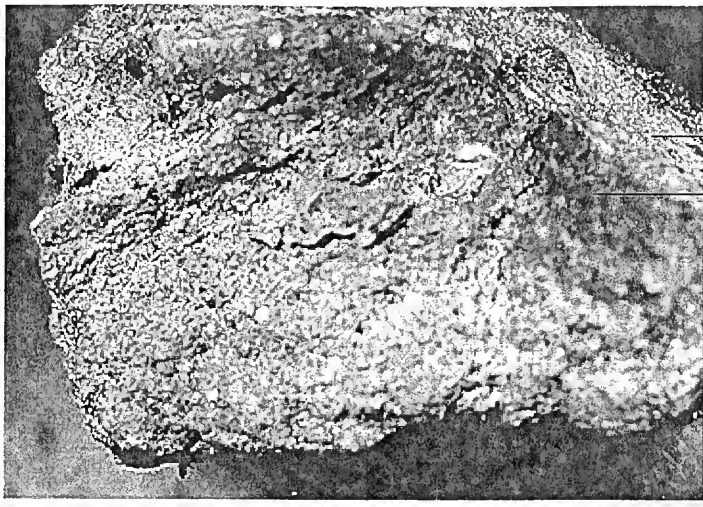


**Figure 15** Deposits on sample from flaked surface, west side

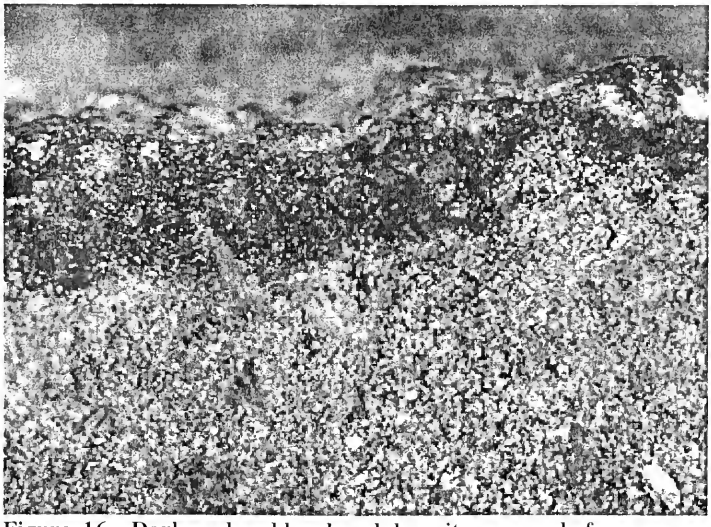

**Figure 16** Darkened and hardened deposit composed of amorphous silica and kaolinite

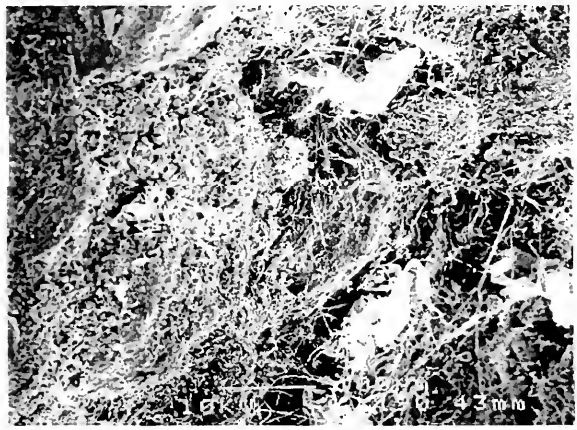

**Figure 17** **Bio growth with kaolinite and gypsum deposits**
**Scanning Electron Micrograph, x 1,190**

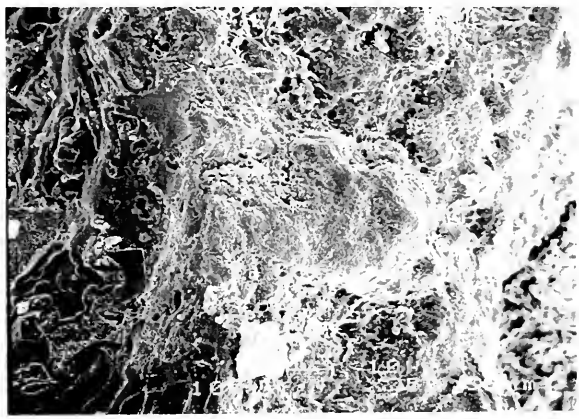

**Figure 18** **Interface of two layers**
**Scanning Electron Micrograph, x 750**

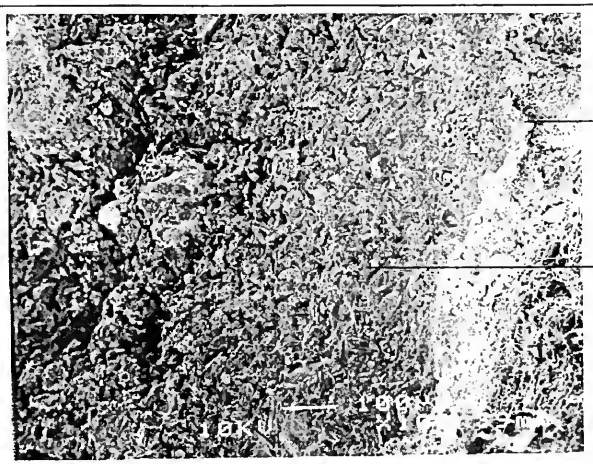


**Figure 19** **Stratigraphy of dense, indurated layer Scanning electron micrograph, x 100**

The samples obtained were fallen pieces of spalled rock. On the opposite side from the depositions, the stone is extremely friable and easily powdered, and was probably caused to spall by extreme disaggregation.

### 4.2.4 Conductance and Qualitative Determination of Salts tests

The test for the qualitative determination of salt initially followed quantities the NORMAL 13/83 Draft Translation standard which specified approximately 100 mg of ground sample to be dissolved in 100 ml of distilled water with known conductance. This test yielded negative results for all salts on the following samples:

1. Powdered surface 5 inches above floor on the west side of wall (PS 1)
2. Powdered surface, 1 meter from floor on west side of wall (PS 2)
3. Deteriorated stone from surface flake on east side (PS 3)
4. Indurated layer from surface flake on east side (PS 4)
5. White efflorescence from dry area, west side (PS 5)

The test was modified by increasing the amount of ground sample to 1 g. in 100 ml. distilled water, and conductance measured a second time. Following are the results:

| SAMPLE | CONDUCTANCE (µs) | CHLORIDES | SULPHATES | NITRATES | NITRITES |
|---|---|---|---|---|---|
| PS 1 | 670 | √ | X | X | X |
| PS 2 | 390 | √ | X | X | X |
| PS 3 | 120 | X | X | X | X |
| PS 4 | 280 | X | √ | X | X |
| PS 5 | 430 | X | √ | X | X |

**Table 1 Results of Qualitative Determination of Salts Test**

There was a higher concentration of chlorides found in the sample taken 5 inches above floor level (PS1) than in the sample taken 1 meter above (PS2). This suggests that salts were transported into the petroglyphs through ground moisture. The high temperature and strong winds on site may have precluded the rise of the salt solution to higher levels on the panel, thus maintaining salt concentration at lower levels of the wall. The gypsum was found in areas above that in which chlorides were found, and was largely concentrated along the surface. This bespeaks of deposition from water percolation rather than capillary rise or traces of previous molding material.

## 4.3 DISCUSSION

Silica and gypsum depositions, and the presence of salts contribute to the deterioration of the petroglyph carvings. Postulations on the origins and mechanisms of these conditions are discussed below.

### 4.3.1 DEPOSITS

KAOLINITE

As in the case of gypsum, kaolinite may also have been used in the moulding mixture. The soil above the shelter may also contain kaolinite constituents which could have been transported by rain. However, the clay is also a common by-product of weathering. Under certain conditions feldspars and volcanic glass can progress through various stages of alteration to ultimately convert to kaolinite.

Clays are among the weakest constituents in a stone, and contribute to its mechanical weakness. These are also highly moisture absorbent, and expand and contract considerably y the action of water and water vapor. The cyclical stresses from their expansive forces within the stone may be sufficient to cause powdering, cracking, or flaking. However, since they are mostly found on the surface, the generation of these stresses cause little detriment to the stone.

INDURATED LAYER

This layer may be likened to a natural consolidant whose protective surface coat is significantly harder than the stone, and thus makes it more able to endure weathering stresses However, as the deposition progresses and the layer thickens, the stone's natural porosity diminishes Although water and moisture permeation through this layer is reduced, the percolation of water and moisture uptake will remain the same. As a result, an increasing amount of moisture accumulates beneath the layer, which accelerates all deleterious effects associated with water: transport of salts, wet-dry stresses, and dissolution of stone constituents

The hardened layer is more widespread than the white deposits. It has coated most of the main panel, including areas close to the carvings and down to the base. By

**Figure 20 Occurrence of spalling close to the carvings**

virtue of its proximity to the carvings, thus exposing the latter to increasing amounts of moisture, it may be said that the presence of, and continued deposition of this layer most threatens the petroglyphs (Fig. 20). The mechanism responsible for the formation of the deposition will be discussed in section 4.2.

### 4.3.2 SOLUBLE SALTS

Salts form by the accumulation of ions leached from stones, soils, mortars and cements and are transported by water. These accumulate in areas where the supersaturated salt solution evaporates, and leaves the precipitated salt. Supersaturation is dependent on the salt phase, and climatic conditions. The deleterious effects of salt are attributed to crystallization, hydration, and dehydration pressures which create strong enough stresses within the pores to pulverize, flake, or spall stone.

#### GYPSUM

Gypsum is a weakly soluble salt ( 257.5 mg /100g water at 20°C) with a high deliquescence humidity at 99.6% that enables it to crystallize even in highly humid environments. It is one of the most common salts found in both natural and man-made environments, such as soils, ground water, stones, mortars, and cements. It has been cited as one of the less destructive salts in comparison to the others, for the associate rate

of decay produced by the presence of this salt in stone is minimal in comparison to decay produced by other salts[21].

Although the white deposits, partially composed of gypsum, occur nearest to the carvings, the deleterious effects of this salt on the tuff is likely to be minimal. This salt is concentrated largely on the outer 2 layers. No gypsum was found in subsurface areas; instead, the bulk of the salt had precipitated and crystallized on the surface. The origin of this salt is very possibly the soil or percolating water from the top of the hill.

Another possible source of the gypsum may be the plaster moldings that were taken for documentation purposes after the discovery of the site in 1965. Plaster of Paris would have been a common moulding material at the time, and its use would explain the proliferation of gypsum deposits on the area of the carvings. However, this cannot be ascertained because as previously stated, materials used and their method of application were not recorded.

### CHLORIDES

Chlorides are more commonly found along coastal regions, such as in the petroglyph site along the Morong Peninsula. This salt group is among one of the more highly destructive types because of it high solubility (37g. Nacl / 100 ml. water at 20°C)[22]

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[21] Konrad Zehnder. "Gypsum Efflorescence in the Zone of Rising Damp" in *Proceedings of the 8th International Congress on Deterioration and Conservation of Stone, Vol 1.* (Berlin: Moller Druck Und Verlag GmbH, 1996). Pp. 1669-1678.

[22] Seymour Lewin. "Susceptibility of Calcareous Stones to Salt Decay" in *Proceedings of the 1st International Symposium on the Conservation of Monuments in the Mediterranean Basin.* Edited by Bari F. Zezza. (Brecia: Grafo, 1990). Pp 59-63.

Consequently, large amounts of salt can be deposited in the stone thus exerting more crystallization pressure. It is likely that petroglyph site tuffs are especially susceptible to these stresses because it is fine-grained and has a high percentage of narrow pores. Moreover, the friability and low tensile strength of the tuff makes it less likely to withstand stresses.

# CHAPTER 5

# ALTERATION BY WEATHERING: CHARACTERIZATION OF QUARRY SAMPLES

In order to confirm the hypothesis that water is the main mechanism that induced the formation of the indurated layer (the condition most directly related to the deterioration of the carvings), the freshly quarried samples were artificially weathered in water. The resulting alteration was analyzed by the same methods used to characterize the petroglyph site tuff. Polarized light microscopy was used to compare visual changes in minerals and matrix between weathered and sound areas of stone. To determine whether ions were leached from the stone during the weathering process, pH and conductance measurements of the water in which the stones were weathered were taken before and after weathering. SEM was used to record changes in morphology, and IR to characterize the deposits which formed during weathering. In addition to the above analyses, the following tests were conducted prior to and after artificial weathering to further characterize the alteration.

## 5.1 PAST STUDIES

Several papers cite the detrimental effects of water on tuffs. The dissolution of glassy constituents are a commonly acknowledged phenomenon in the study of this stone (Fratini et al, 1994), (Helmi, 1994), (T. Topal, V.Doyuran, A. Turgmenoglu, 1995), (Wendler, Charola, Fitzner, 1996) (De Witte, et al, 1988) (R. Rossi-Manaresi and G.Chiari, 1980) Of particular importance is Helmi's and Wendler, Charola and Fitzner's

work. The former examined the weathering of tuff under similar conditions as those used in this study. It was found that aging cycles caused rapid weathering in samples due primarily to the leaching of iron, calcium and sodium, and traces of potassium and magnesium from glass matrix, which resulted in increased porosity. These elements were re-deposited in pits and cavities on the surface of samples. The development of glass also played an important role in the surface color change in stones. The latter study weathered two types of tuffs, and observed an amorphous silica precipitate that resulted from the dissolution of glassy constituents.

The development of a certain pore class has also been cited in two other studies. F. Fratini et al. report an increase in small pores, ranging from $10^4$ and $10^5$ Å, and attribute this to the hydrolysis of the vitreous matrix. Wendler, Charola, and Fitzner likewise cite the growth and decline of certain pore groups among fine grained and coarse-grained samples. They postulate that this is due to a two-step process during the hydrolysis: first is the increase in number of larger capillary pores caused by dissolution of the vitreous matrix and losening of lapilli from their matrix, followed by the re-deposition of the glassy material within the pores thus reducing number of large capillary pores and increasing that of smaller capillaries.

The use of feldspars as an indicator for depth of alteration due to weathering follows a study of the deterioration of tuffs from the Goreme Valley, Turkey. Here, the weathing of feldspars, cross-checked by the study of biotite alteration and SEM analysis, proved to be consistent with the weathering the other analyses. (Caner-Saltik, et al, 1995), (Topal, Doyuran, and Turkmenoglu, 1995).

The work analyzing the causes of disaggregation of tuff from Cochasqui, Ecuador, (R. Maneresi, and A. Tucci, 1994) cites the heavy rainfall and significant quantity of pores with radius <.05 μM, which allow moisture adsorption. The destructive mechanism in this process is the pore saturation by molecular water, which is rigid enough to exert sufficient pressure against the walls. When this pressure exceeds the material's tensile strength, disaggregation and flaking occur. Pores saturated with molecular water also take a longer time to evaporate than bulk water, thus impeding the passage of the latter and hastening the process of deterioration.

L. Lazzarini, et al. (1996) report the zeolitization of the glassy matrix due to the chemical action of rain water. Found in both petroglyph site and freshly quarried samples, the presence of these minerals could play a role in overall deterioration. A. Colantuono, S. Dal Vecchio, and O. Marino (1990) studied the relationship of cyclic dimensional changes in tuffs to the stone's properties, and concluded that zeolitized tuffs showed a lower drying rate and greated and quicker dimensional changes than unzeolitized tuffs. This signifies that the presence of zeolites, aside from increasing the ion exchange properties in the stone, are likely to increase stresses by expansion and contraction.

## 5.2 ANALYSES: MICROSCOPY, IR SPECTROSCOPY, CONDUCTANCE AND PH, COLOR

### 5.2.1 MICROSCOPY

There is a slightly higher percentage of rock fragments than in the petroglyph site tuffs: the matrix is approximately 65%, and the remaining 35% are rock fragments of pumice, basalt, and scoria. The matrix is composed of approximately 60% glass, a slightly lower percentage than that of the petroglyph site tuff. Feldspars are the predominant mineral, comprising about 15% of this stone. These occur as tiny fragments of 0.05 mm to 1 mm. Clay content is negligible.

Rock fragments in the buff-brown quarry stone are dominated by white, black, and brown pumice, and to a lesser extent, basalt clasts, set in an unwelded, vitric matrix. Clast size ranges from coarse lapilli to fine ash, depending on fragment type and color. The dark brown / black pumice clasts range from 65mm, the light brown pumice from 6 - 25 mm, and the white clasts vary least, at 1.5 mm. Basalt ranges from 1.5 to 20 mm.

Alteration due to artificial weathering is visually apparent when contrasting weathered areas with sound stone. Weathering due to hydrolysis was evidenced by the following observations: 1) surface erosion of the stone (Fig. 21), 2) lightening of the darker colored areas of the matrix and glass fragments, as seen under uncrossed polars and (Figs. 22-25), 3) widening of cleavage planes in feldspars as observed under crossed polars, and, 4) the fading of a crystalline boundary around pores. These changes are most distinct closest to the surface and diminish with increasing depth, ultimately ceasing at a depth of approximately ½ inch.

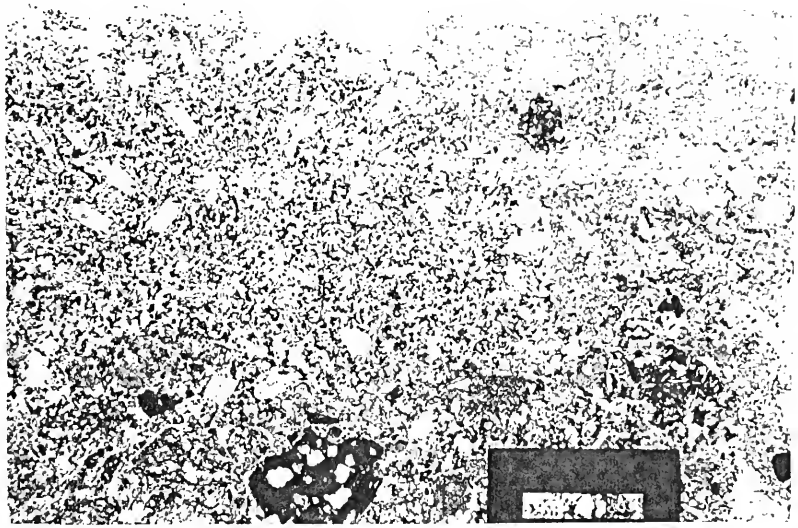

Figure 21 Physical erosion of surface of artificially weathered stone
Polarized light micrograph, uncrossed polars, x 25

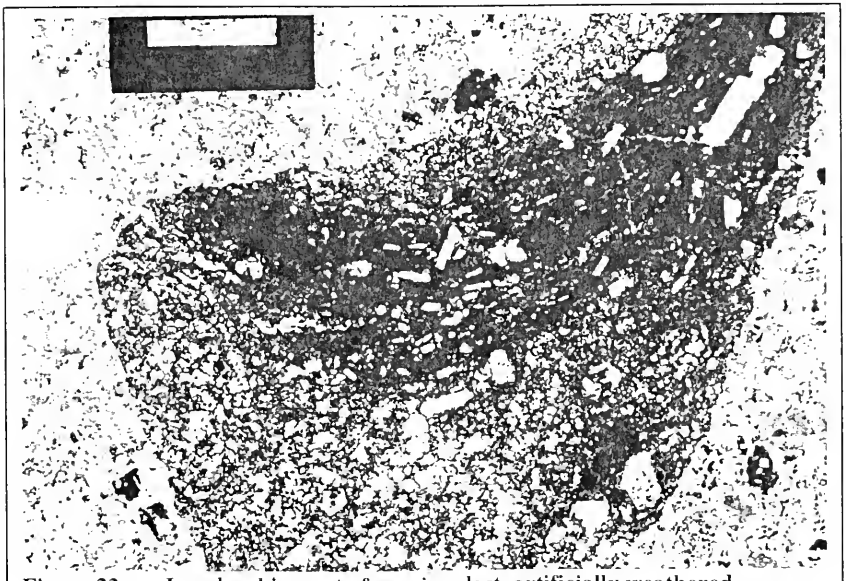

Figure 22 Iron leaching out of punice clast, artificially weathered
Polarized light micrograph, uncrossed polars x 25

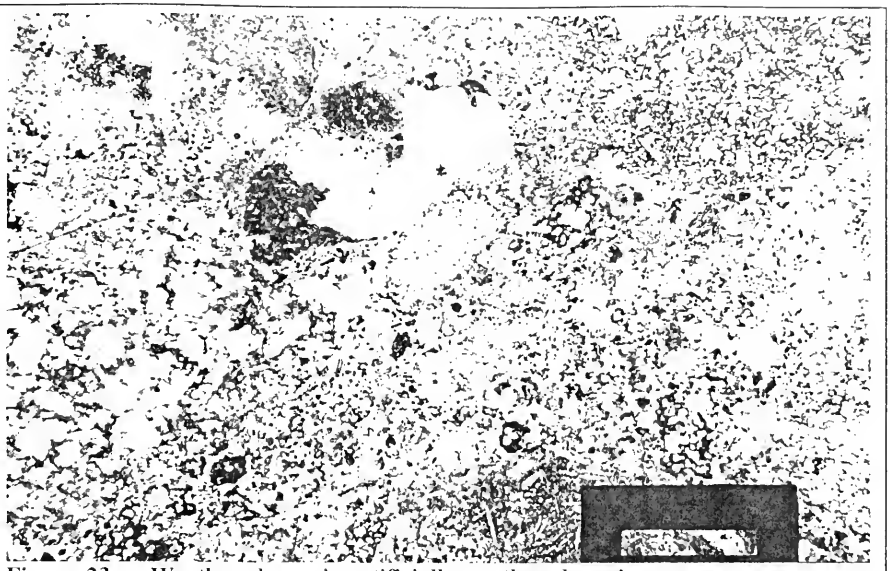

Figure 23 Weathered zone in artificially weathered specimen
Zone is significantly lighter than sound areas (Fig. 24) due to leaching of iron. Polarized light micrograph, uncrossed polars, x 25.

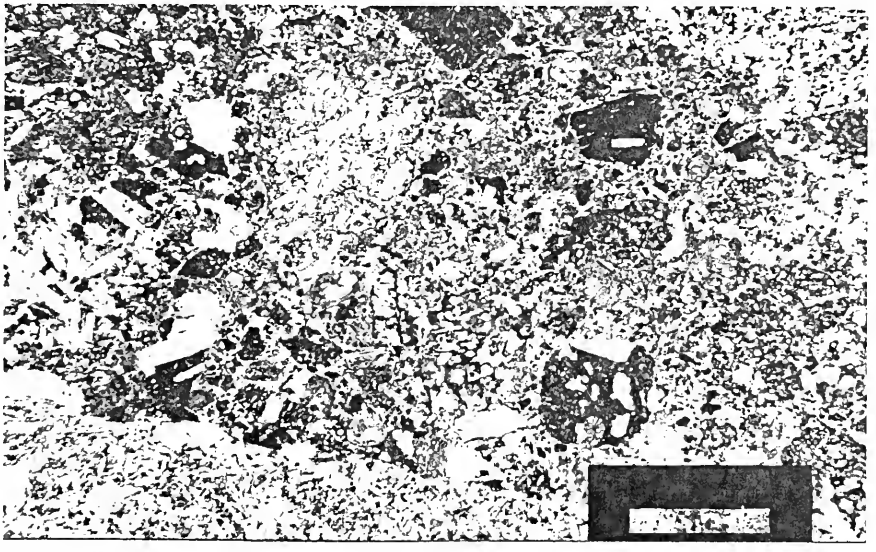

Figure 24 Sound area in artificially weathered stone.
Area is darker from higher iron content.
Polarized light micrograph, uncrossed polars, x 25.

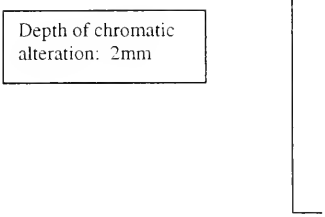

**Figure 25 Chromatic alteration close to surface Artificially weathered stone. Polarized light micrograph, uncrossed polars, x 25**

Weathering is evidenced in darker glassy areas of the matrix and rock fragments such as pumice and scoria. These diminish in color from a deep dark brown to a light yellow brown as they near the surface (Figs. 22 to 25). The dark color is due to the presence of iron in the glass, and the loss of this element results in the loss of color in the material. Because the iron is chemically bound to other elements that collectively form the glass, the leaching of this element necessarily includes the leaching of others, which may include silica, magnesium, and potassium. Prolonged hydrolysis of these minerals may explain the formation of the darker, hardened surface in the Angono petroglyph samples. Suspended in solution, the altered

forms of these elements migrate towards the surface, ultimately resulting in a precipitated deposition. Thus the hardening of the layer may be caused by the consolidating action of silica and other minerals in the pores and interstices of the stone, and the darkening of the layer from the concentration of iron in the precipitate.

Another manifestation of weathering is the alteration of feldspars, which has been an effective gauge to assess the depth of weathering in tuff through observation of cleavage planes.[23] This mineral exhibits change relatively rapidly in comparison to other minerals. Common by-products of the weathering of this mineral are kaolinite, hydrated silica, and alumina (when hydrolyzed by sea-water). Lastly, the crystalline boundary that delineated the pores in unweathered samples was not observed after weathering.

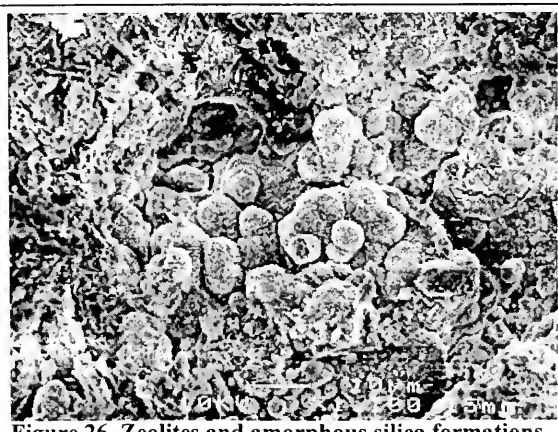

**Figure 26 Zeolites and amorphous silica formations**
**Artificially weathered sample**
**Scanning Electron Micrograph, x 1,100**

When analyzed under SEM, both weathered and unweathered specimens showed the presence of amorphous silica formations and zeolites. (Fig. 26). Slight erosion was observed around basalt rock fragments, and to a lesser extent around light

[23] Caner-Saltik, et al. "Examination of Surface Deterioration of Goreme Tuffs for the Purpose of Conservation." In *The Safeguard of the Rock-Hewn Churches of the Goreme Valley, Proceedings of an International Seminar.* (Rome: ICCROM, 1995) pp. 84-93.

brown pumice clasts. Artificial weathering accelerated erosion, especially around basalt and pumice clasts, and in some cases fractured the pumice. There was also a higher incidence of microcracking in weathered samples, as evidenced through SEM.

### 5.2.2 IR Spectroscopy

One of three weathered specimens developed a whitish surface deposit at the corners and of the cube (Figs. 27 & 28). The substance was scraped off the cubes and subjected to IR analysis, which revealed it to be an amorphous silica (see appendix for IR spectra). This supports the hypothesis that water causes the leaching of siliceous substances, migration to the surface and subsequent precipitation. The spectrum band of

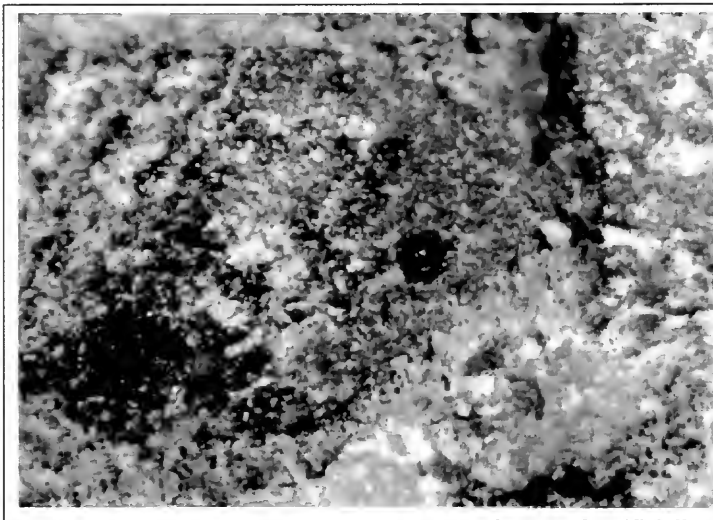

**Figure 27 White deposits collected in recessed areas of artificially weathered sample**

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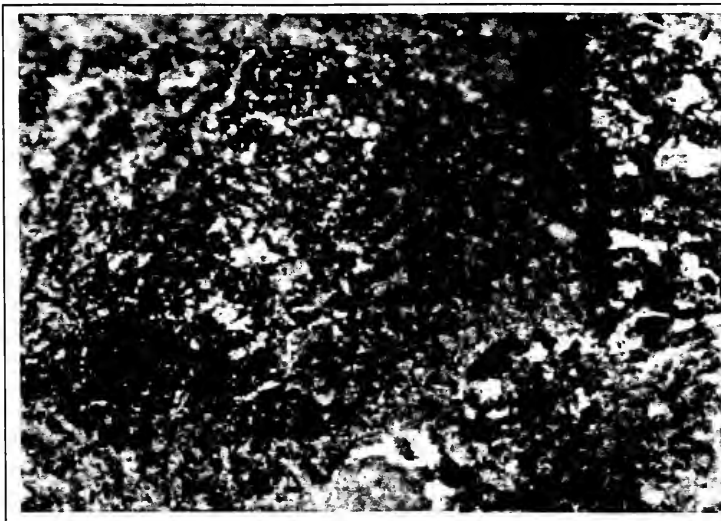

**Figure 27 White deposits collected in recessed areas of artificially weathered sample**

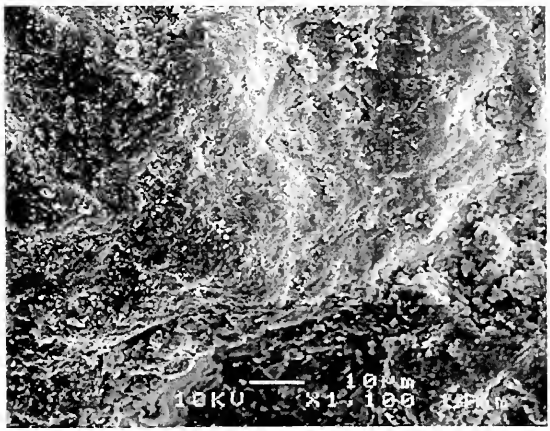


**Figure 28 Amorphous silica deposit on surface of artificially weathered samples. Scanning Electron Micrograph, x 1,100**

this white efflorescence is very similar that of the petroglyph site's subsurface deposit, which would confirm that the surface hardening on the site was also caused by the action of water.

### 5.2.3 CONDUCTANCE AND pH

Evidence of the leaching action from minerals is reflected in the change in pH and conductance readings of the water in which the stones were weathered. The dissolution of stone constituents increased conductance readings from 0μS (de-ionized water prior to weathering) to 190μS. The ions in the water that were leached out of the stone during weathering confirm the material loss and solubilization of the tuff.

An increase in pH in the distilled water from 4.65 prior to weathering to a less acid 6.90 indicates the nature of dissolved material from which these ions originated. Volcanic glass is a likely origin, for it has a high concentration of alkali ions which are commonly released during initial stages of dissolution.[24] This is supported by the findings of Fratini, et al (1994), who noted a decrease in concentration of alkali ions of the

[24] R.V. Fischer and H-V. Schmincke. *Pyroclastic Rocks.* (New York: Springer-Verlag, 1984) pp. 327.

vitreous matrix in weathered stones. Another source may be the feldspars, which release silica, alumina, and alkalies as they decompose.[25] Hence both glass and feldspars are the most probable sources of leached ions in the water, which is further supported by changes previously mentioned in this section. The hypothesis was verified evaporating the water in a well slide, and subjecting the evaporate subjected to IR analysis. Results show the evaporate to be an amorphous silica

### 5.2.4 COLOR

Stones exhibited a slight color change from a yellow-brown tone (Munsell 10 YR 4/1) in their unweathered state to a lighter brown with bluish-gray tone (Munsell 10 YR 5/1) in the weathered state (Fig. 29). Loss of the brown color may be a result of the leaching of iron, as was shown through petrographic analysis. Although the white deposits may contribute to the color change, the chromatic alteration was observed even in samples that did not exhibit the silica deposits.

## 5.3 POROSITY :

#### CAPILLARY ABSORPTION, TOTAL IMMERIOSN, AND DRYING BEHAVIOR

All stones exhibited consistent weight loss after artificial weathering, signifying that the wet-dry-high humidity cycles deteriorated the tuff. Porosity increased by a range of 0.85% to 1.35% per specimen, and average specimen weight decreased by 0.6 g. or 0.34% of total weight. This is attributed to both disaggregation and dissolution of the stone in water (Table 2).

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[25] F.C. Loughnan. *Chemical Weathering of Silicate Minerals.* New York: American Elsevier Publishing Company, Inc., 1969) p. 29.

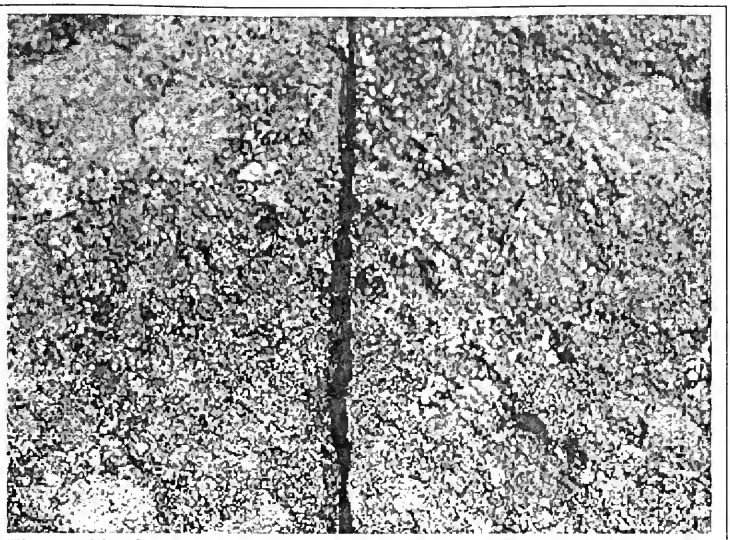

Figure 29 Chromatic alteration between unweathered (left) and weathered specimens (right)

| Property | Unweathered | | | Weathered | | | Difference | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | A | B | C | A | B | C |
| Dry Weight (g.) | 176 | 185 | 178.4 | 175.4 | 184.3 | 177.8 | -0.32% | -0.38% | -0.32% |
| Saturated Wt. By Capillary Absorption (g.) | 232.3 | 243. | 234.5 | 233.7 | 244 | 236.3 | 0.49% | 0.40% | 0.77% |
| Saturated Weight by Total Immersion (g.) | 233.7 | 244.3 | 235.6 | 236.4 | 246.4 | 238.7 | 1.11% | 0.86% | 1.35% |
| Difference in absorbed water by 2 methods (g) | 1.23 | 1.29 | 1.06 | 2.7 | 2.4 | 2.4 | 117.89% | 88.37% | 129.25% |
| Capillary Absorption Coefficient ($g/cm^2 \cdot s^{1/2}$) | 0.028 | 0.039 | 0.022 | 0.017 | 0.026 | 0.015 | 39.3% | 33.3% | 31.8% |
| % Porosity (using total immersion) | 32.8% | 32% | 32% | 34.7% | 33.7% | 34.3% | 2% | 1.6% | 2.3% |

**Table 2. Summary of results of capillary absorption and total immersion tests**

During the artificial weathering process, the stone samples disaggregated and loose particles were found in the water. In order to quantify the stone loss by disaggregation, particles were sieved through a 300 μm mesh and dried to constant weight. Total weight of disaggregated particles from the weathering of 3 test specimens

plus one control specimen was 0.47 g. Thus total weight loss from the 3 samples (1.84g) less the weight of disaggregated particles from 4 samples (0.47 g) gives an estimate of stone loss which may be attributed dissolution in water (> 1.37 g.). The figure for weight loss due to disaggregation may have a larger error because this includes loss from physical handling of specimens during weathering.

### 5.3.1 Capillary Absorption

A consistent increase in saturated weight ranging from 0.40 % to 0.77% (See appendix for capillary absorption tables). The increase in porosity, which reflects an altered pore structure, is evidenced by a 3.3% average increase in quantity of water absorbed and a 35% decrease in rate of water absorption by capillary action (capillary absorption coefficient) after weathering (Fig. 30 a, b & c). Total saturated weight increased across all samples by an average of 0.55%. These occurences may be explained by an altered pore structure. Because the rate of rise is directly related to pore size, a shrinkage of pores will decrease the velocity of rise.[26] Thus a probable effect of weathering by water is an increase in porosity via the formation of a finer pore network.

The hypothesis of pore shrinkage by deposition of silica and other insoluble residue by water action is supported by the decrease in capillary absorption coefficients and increase in saturation weights by total immersion for the weathered with respect to the unweathered sets (Table 2).

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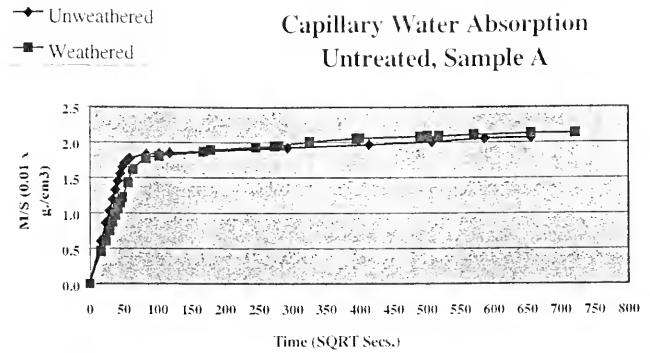
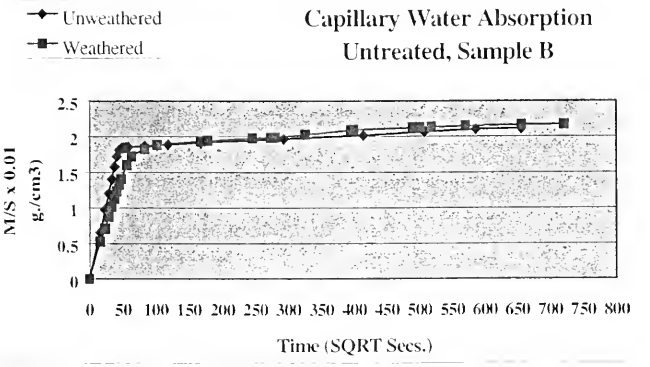
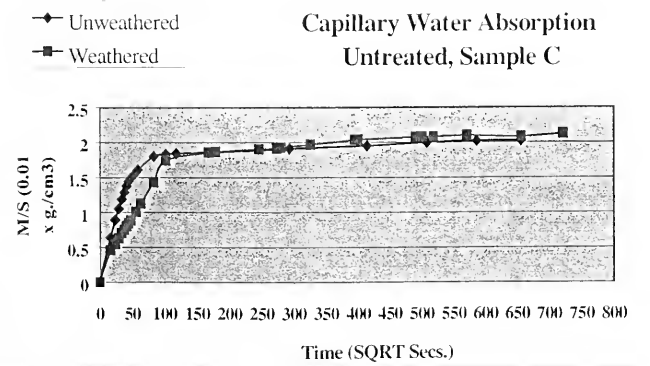
[26] Seymour Lewin. "The Mechanism of Masonry Decay Through Crystallization." In *Conservation of Historic Stone Buildings.* (Washington, D.C.:National Academy Press), 1982. Pp. 120-144.


Unweathered
Weathered
Capillary Water Absorption
Untreated, Sample A
M/S (0.01 x g./cm3)
2.5
2.0
1.5
1.0
0.5
0.0
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800
Time (SQRT Secs.)


Unweathered
Weathered
Capillary Water Absorption
Untreated, Sample B
M/S x 0.01 g./cm3)
2.5
2
1.5
1
0.5
0
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800
Time (SQRT Secs.)


Unweathered
Weathered
Capillary Water Absorption
Untreated, Sample C
M/S (0.01 x g./cm3)
2.5
2
1.5
1
0.5
0
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800
Time (SQRT Secs.)

**Figs. 30, a,b, & c.**

### 5.3.2 TOTAL IMMERSION

A small increase in saturated weights from capillary absorption to total immersion signifies a high rate of absorption by capillary action. That is, open pores are accessed by water through capillary rise so that the incremental pore space filled through total immersion is minimal. Conversely, a large increase in saturated weights indicates less capillaries available for absorption by capillary rise, requiring total immersion to fill them.

In the unweathered set, stones gained an average of 1.2g more water by total immersion after having been fully saturated by capillary action. This difference was larger in weathered samples, which increased by an average of 2.5 g. That the weight increase doubled suggests not only an increase in porosity, but also the development of a finer pore network that inhibits water uptake by capillary action. The open pores unfilled by capillary action were filled during total immersion, reflecting the increase in saturation weights.

### 5.3.3 DRYING BEHAVIOR

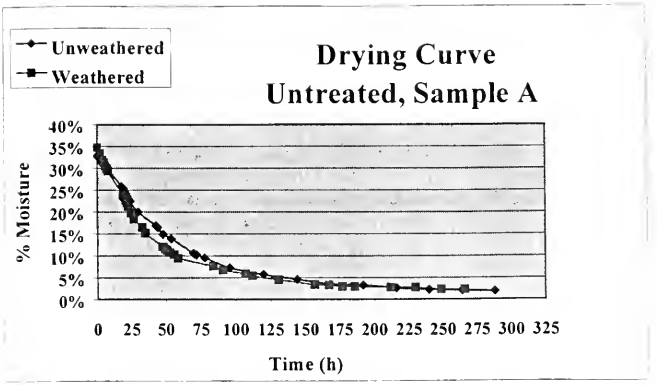
The drying rate consistently increased across all samples after weathering (Figs.31 a,b,c), and is evidenced in the 31% average increase in initial drying rates at 22 hours (Table 3). This may be explained by an increase in porosity as a result of weathering. A higher percentage of open pores signifies more open paths by which water may evaporate, raising the rate of release of water and water vapor. It has been suggested that faster drying may also increase the stress from quicker transitional stress from its wet to dry state, potentially resulting in fissures and microcracking (Rossi-Manaresi and

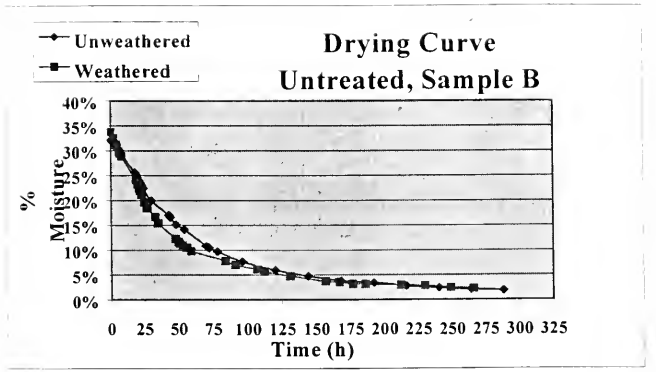
Tucci, 1994). However, the stress generated by faster drying is likely to be low because clay content is negligible. Also, the presence of zeolites is not likely to greatly stress the stone, because detrimental expansion and contraction due to zeolites is accompanied by an increased drying rate,[27] which was not observed here.

| Samples | Initial Drying Rate Coefficient % moisture lost (g.) / Time | | |
|---|---|---|---|
| | A | B | C |
| Unweathered | -0.0042 | -0.0039 | -0.0041 |
| Weathered | -0.0055 | -0.0051 | -0.0052 |

**Table 3. Drying rate coefficients for untreated samples.**

[27] A. Colantuono, S. Dal Vecchio and O. Marino. "Accurate Measurement of Expansion and Shrinkage in Porous Stones Caused by Moisture Absorption." In *Conservation of Stone and Other Materials, Vol. 1.* Edited by M.-J. Thiel. (London: E. & F.N. spon, 1984). Pp. 204-211.



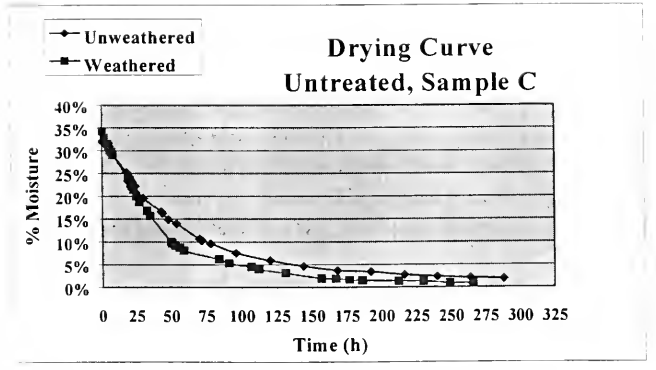




**Fig. 31, a,b,c. Drying curves for untreated samples.**

## 5.4 MECHANICAL TESTS

### 5.4.1 COMPRESSIVE STRENGTH

There was no discernible difference in compressive load bearing capacity between unweathered and weathered samples. Plastic limit in the unweathered set ranged from 1.05 to 1.4 psi, while that of weathered samples ranged from 1.1 to 1.55 psi (Table 4). However, while permanent deformation occurred at almost the same loads, elasticity varied between the two sets. Elasticity is indicated by load relative to the time during which load is applied but the material does not yet reach permanent deformation. An increase in duration before which plastic deformation occurs is reflected by a lower slope which indicates greater elasticity, while a decreased duration is reflected by a higher slope, signifying brittleness (Fig. 32).

| Samples | Time (Minutes) | Load (psi) |
|---|---|---|
| Unweathered, Untreated | | |
| A | 57 Secs. | 1,250 |
| B | 1 Min. | 1,400 |
| C | 33 Secs. | 1,050 |
| Weathered, Untreated | | |
| A | 1 Min. | 1,200 |
| B | 1 Min. | 1,550 |
| C | 1.30 min. | 1,100 |

**Table 4. Results of compressive strength tests indicating plastic limit (load) and elasticity (time)**

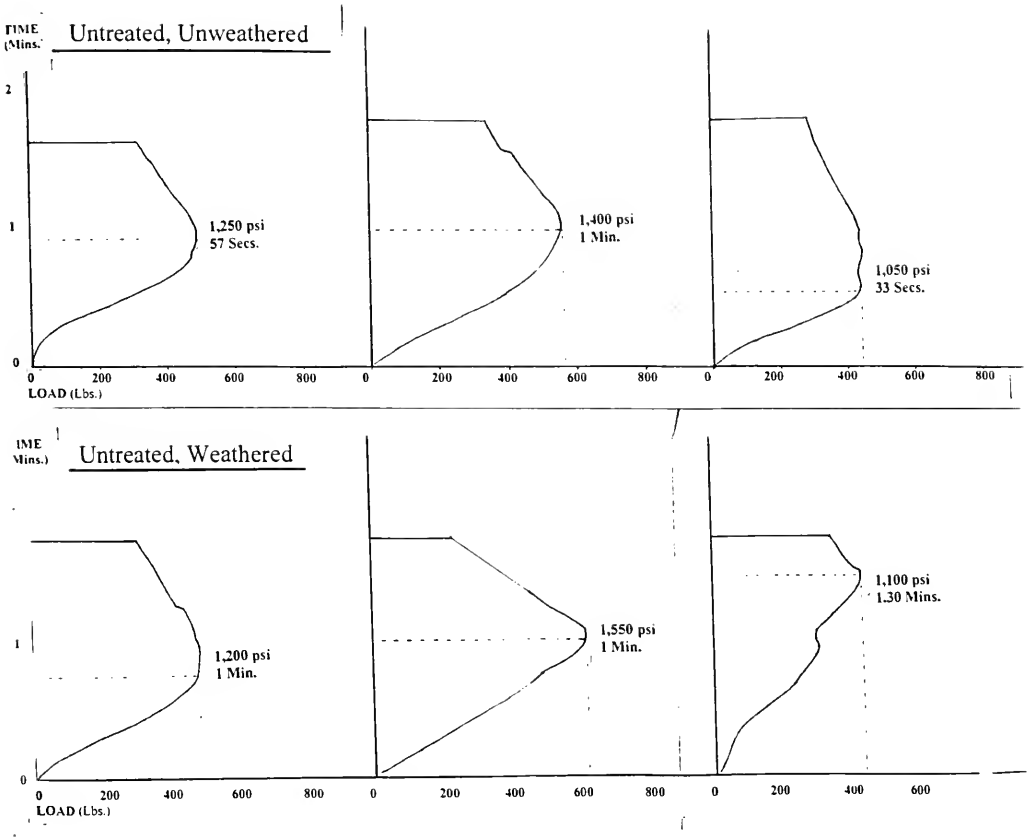



**Fig. 32 Compressive strength graphs**

Two out of three samples in both unweathered and weathered sets reached their plastic limits at approximately 1 minute; the remaining unweathered specimen reached this limit after 30 seconds, while the weathered specimen reached this point after 1 minute and 30 seconds. The difference between these latter two specimens, seems to

suggest that weathering increases the material's elasticity. However, a lack of consistent results across all samples shows that this is insufficient data to reach conclusions on the effect of weathering on the compressive strength. The disparity in results between the two sets may be attributed to the inherent inhomogeneity of the stone, uneven sample preparation, and / or a decrease in strength due to weathering.

### 5.4.2 THREE POINT BENDING TEST

Unweathered samples reached their plastic limit between 91 to 131 lbs. (Table 5). This range is greater in weathered samples, which varies from 30 to 128 lbs. The increase in range of plastic limits may reflect either the inherent heterogeneous nature of the sample, or the decreased the bond strength due to weathering which weakens it along certain paths.

Samples increased in elasticity after weathering (Fig. 33), which is evidenced in a higher average displacement value relative to load compared to unweathered samples (A higher displacement figure signifies greater elasticity, and a lower figure, brittleness). Because treated samples showed more consistent results than those in the compressive strength test, it is more likely that the difference between unweathered and weathered samples is due to weathering than inhomogeneity of samples or inaccuracies in sample preparation.

| Untreated Unweathered | Displacement (Inch) | Load (Lb.) |
|---|---|---|
| 1 | 0.0045 | 421 |
| 2 | 0.0062 | 606 |
| 3 | 0.0062 | 536 |
| 4 | 0.0065 | 573 |
| Untreated Weathered | | |
| 1 | 0.0045 | 592 |
| 2 | 0.0037 | 139 |
| 3 | 0.0057 | 398 |
| 4 | 0.0037 | 555 |

**Table 5. Results of three-point bending tests indicating plastic limit (load) and elasticity (displacement)**

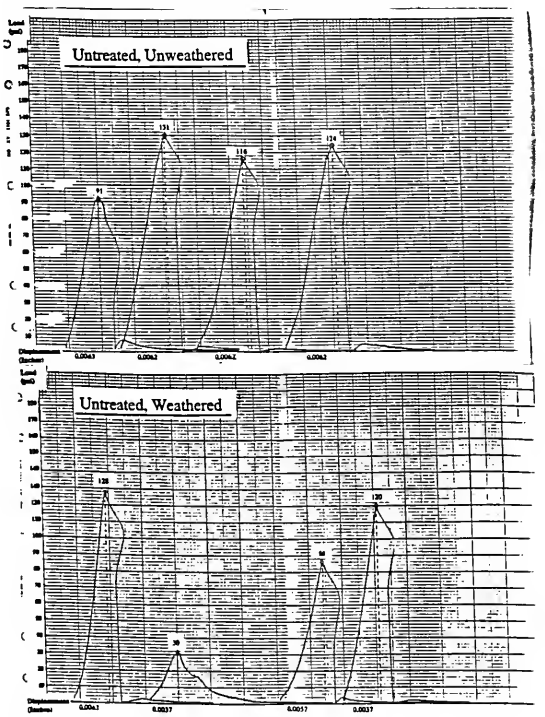



**Fig. 33. Chart for 3-point bending test**

### 5.4.3 Discussion

Because the results of mechanical tests were not consistent across all samples, the interpreted embrittling of the material may be due to other factors than the weathering process. The heterogeneous nature of the stone, compounded by the small sample size and sample preparation are also a likely cause of the inconsistent results. Because tuff is composed of a variety of clasts of different sizes, each type will have a have different compressive strength. The degree to which it influences the overall compressive strength of the stone depends on its size and distribution throughout the stone in relation to the other clasts and matrix. Given that there are various types and sizes of clasts which are unevenly distributed in the stone, inconsistent results in compressive strengths may well be a reflection of this inhomogeneity. Sample preparation may also have some bearing on the results. Samples should ideally be perfect cubes. A slight difference in height resulting in an uneven surface, or chipped edges may cause inaccurate calculation of the compressive strength due to preferential concentration of the load on the elevated end of the sample, or in the weaker areas.

However, weathering by water may have altered the plasticity of the stone, causing brittleness in weathered samples. Since the strength of a material is only as high as the strength of its weakest bond, the lower loads that caused the mechanical failure of the stone may be indicative of this preferential weakening. Findings of increased porosity and higher incidence of microcracks in the weathered sample support this conclusion.

## 5.5 Comparison of Artificially and Naturally Weathered Tuff

### 5.5.1 Summary

The main effect of weathering is the leaching of silica, iron and other alkali ions from the vitreous matrix and clasts which dominate the overall composition of the stone. This dissolution is the basis of alteration of other properties, such as color change, increased porosity and rate of drying, a higher incidence of small pores, and mechanical weakening by embrittlement.

The alteration of these properties in turn accelerates the weathering process. A higher porosity increases the stone's capacity to absorb water. This, coupled with an increase in small pores (which enables prolonged retention of water) and the stone's inherently fine particle size, will give rise to a higher specific surface area. This furthers the adsorptive capacity of the stone. In particular, if the pore size should fall below 0.05μm, the maximum diameter in which adsorption of liquids and gases occurs. With an increased capacity to absorb and retain water, the cycle is repeated, causing further alteration of the cited properties, whose net result is a faster deterioration rate.

Increased porosity also increases the rate of drying, but any increase in stress due to wet-dry cycling may not be too significant due to the low amounts of clays present. These, however, will increase with prolonged weathering.

Some effects of wetting and drying stresses could be microcracking and erosion along preferred paths by water. Both occurences embrittle certain areas in the stone and diminish its overall mechanical strength.

### 5.5.2 DISCUSSION

Glassy volcanic rocks are one of the most easily altered rock types. Their instability is due to rapid cooling in their magmatic state, allowing little time for the silica to form an orderly crystalline structure. The result is a loosely arranged silica network with substantial intermolecular space into which extraneous substances may enter.

The most deleterious substance to volcanic glass is water. In initial stages of hydrolysis, a diffusion controlled hydration and alkali ion exchange occurs, but with relatively minor chemical change. A destruction of the matrix, and the precipitation of dissolved glass into pore spaces commonly follows this first stage. The glasses have a high initial alkali content, which is release into the solution and generate high pH conditions under relatively closed system conditions,[28] such as in the weathering carried out in this study.

Because pH levels determine the relative solubility of minerals, dissolution of one will necessarily affect the rest. In a weakly acid water of pH 4.5 to 6.5, $SiO_2$ may be immobilized, forming either clay minerals or fine-grained mixtures of gibbsite and quartz, or its solubility will proceed at a very slow rate. As the system becomes increasingly alkaline, however, $Al_2O_3$ and $Fe_2O_3$ may be removed in solution, and more or less of the $SiO_2$ will be precipitated.[29] This sequence may explain the manner in which the volcanic glass has dissolved.

The formation of the amorphous silica deposits on the surface of only one of the

[28] R.V. Fischer and H-V. Schmincke. *Pyroclastic Rocks.* (New York: Springer-Verlag, 1984) pp. 327.
[29] W.D. Keller. *Principles of Chemical Weathering.* (Missouri: Lucas Brothers Publishers, 1968), pp.26-28

three weathered samples suggests that only one of these stones had the higher percentage of vitreous substances, higher porosity, and other properties that would make it more susceptible to attack by water.

## 5.6 CONCLUSION

IR analysis of deposits that formed on both artificially and naturally weathered tuff indicate whether or not these conditions were caused by wet-dry-high humidity cycles. The presence of kaolinite on petroglyph samples and their absence in artifically weathered quarry samples suggest either that 1) this is due to past documentation via molding, and not the action of wet-dry-and high humidity cycles, 2) kaolinite was formed by wet-dry cycles in conjunction with other mechanisms, (such as large mineral concentrations in the soil above the site), 3) these are formed by the mentioned cycles, but that differing minerals are produced by the same weathering stimuli is due to subtle differences in mineralogy between the two stones, or 4) the minerals are formed only by wet dry cycles, but take a longer time to form than the time allotted in this study. The gypsum may likewise have originated with the moldings, and / or originated from its many natural sources.

A common condition to both artificially and naturally weathered samples is the deposition of amorphous silica on stone surfaces. That this substance was generated in some freshly quarried tuffs by exposure to wet-dry-high humidity cycles signifies this condition was caused by the action of water. Conductivity, pH, IR and porosity and drying index tests on artificially weathered samples further support the hypothesis that the silica had indeed dissolved, and were transported within the pores.

In the petroglyph samples, the silica forms an indurated layer, which has been shown to pose a threat to the conservation of the carvings since it reduced porosity. In the artifically weathered samples, the silica forms a white deposit. The similarity of amorphous silica spectra in both the petroglyph site and quarry samples indicates that the white effloresences produced in the latter will ultimately progress to form the more detrimental hardened layer that threatens the carvings.

The crystalline boundary that was observed in unweathered quarry samples but not in weathered samples was also absent in the petroglyph site samples. This suggests that weathering had caused the band to fade or dissolve.

Although it appears that the same mechanism produced similar conditions in both sets, it is likely that the other observations based on tests conducted only on the quarry tuffs, such as increased porosity, formation of finer pores, increased elasticity and color change apply to initial stages of weathering. Over ten thousand years, as is the case of the petroglyph samples, results such as an increased drying rate would be different during the later stages of weathering because of the increased deposition of silica. Thus the increase in drying rate only reflects increased porosity. Futhermore, the artificial weathering was conducted in a controlled environment with only two variables for stimuli. The mechanisms affecting deterioration on site are far more, and have still not yet been thoroughly studied. Factors such as pH of percolating water, presence of soluble salts, microclimate, lichens, bio growth, animal activity, effects of tremors both natural and anthropogenic, and pollution will affect the interrelated causes and effects on the stone.

However, other conditions based on the results from the artificially weathered quarry samples may be deduced to apply to the petroglyph site. Color change caused by the leaching of iron, which is chemically bound to leached silicates, may explain the darkening of the hardened amorphous silica deposit in the Angono petroglyphs. Dissolution of vitreous constitutents caused the formation of finer pores and increased porosity which would have furthered the stone's susceptibility to the detrimental effects of water and soluble salts. Other conditions such as such as microcracking and embrittlement, which are due to disaggregation and dissolution are directly observed in the friable, spalled samples of the petroglyph site, and the decreased mechanical strength of the quarry samples, thus ascertaining that these are caused by the wetting and drying. It must be noted that petroglyph site's weathered conditions which were attributed to the action of water could have been compounded by other mechanisms on site in conjunction with the water, such as biological growth and salts.

# CHAPTER 6
# EVALUATION OF THE CONSOLIDANT

The efficacy of Conservare OH Stone Strengthener as consolidant for this tuff was evaluated according to its ability to deter or delay the generation of deteriorated conditions which were observed in weathered, untreated stones and its compliance with criteria listed in section 3.4. Because both treated and untreated specimens were weathered under the same controlled conditions and subjected to the same tests and analyses, consistent differences between the two sets may be attributed to the consolidant. Following are the results obtained.

## 6.1 PAST STUDIES

Few studies have been able to report on long-term evaluations of the on-site weathering of tuffs consolidated with silicate esters. The study that covers perhaps the longest term performance of the consolidant on a tuff, is also the most optimistic of reports. L. Lazzarini et al. (1996) cite the "satisfactory state of preservation"[30] of a Moai statue consolidated with Wacker OH ten years ago. It must be noted that the deterioration of the Moai is caused by water, and the statue has weathered in a sub-tropical environment. The treatment cited in this study was applied by B. Prieto, who included observations in a later study (B. Prieto, 1994). The study cites that Wacker OH produced homogeneous consolidation. When testing the consolidant on site, however, she

[30] Lorenzo Lazzarini, et al. "New Data on the Charaterisation and the Conservation of the Easter Island's Pyroclastics Used for the Moais" In *Proceedings of the 8th International Congress on the Deterioration and Conservation of Stone.* Edited byJosef Reiderer. (Berlin: Moeller Druck & Verlag, 1996) pp. 1147-1152.

found that the solvent evaporated too quickly, and caused the silica to precipitate on the surface. Another study by De Witte, (1995) lab tested the efficacy of Tegokavon and Wacker OH on the Göreme rock from the rock cut churches, Turkey after weathering by water. He found both performed equally well in the prevention of erosion of the glassy matrix. Tegokavon was then applied on a test area on site. After five years, there was no discernible difference between treated and untreated areas; both had eroded to the same depths. SEM examination showed no trace of the siliceous polymer on the stone's surface.

Wendler, Charola, and Fitzner (1996) weathered treated stones by water for 300 days, and found that consolidation by Wacker OH did not prevent the formation of amorphous silica deposits which were observed on site. They also found that the cracking of the rigid gel of the consolidant formed additional micropores that increased the stone's capacity for water vapor transmission.

The polymerization of the consolidant MTMOS under different relative humidities was studied by Charola, Wheeler, and Freund (1984). The curing of this compound undergoes the same steps during polymerization as a silicate ester, thus results could be applicable to the curing of the latter, although catalysts will diminish the effect. It was found that the consolidant completes the hydrolysis stage when cured under 100% RH, but undergoes only partial condensation, resulting in a rubbery polymer which exhibited substantial cracking. As RH decreases, less of the consolidant completes hydrolysis, and commensurately more undergoes condensation. This produces a less elastic polymer, which increases in brittleness but decreases incidences of cracking as RH diminishes.

## 6.2 Analysis: Depth of Penetration, Microscopy, Conductance pH, and Color

### 6.2.1 Depth of Penetration

Depth of penetration was determined by the iodine vapor technique,[31] which stains the polymerized consolidant a faint yellow brown by adsorption of sublimated of iodine crystals in a closed chamber. The concentration of polymerized product on the stone is indicated by intensity of the stain: a more pronounced stain signifies a high amount of polymerized consolidant, while a weaker stain indicates either a lower amount of consolidant, or lesser degree of polymerization. Staining is normally detected within minutes in lighter colored stones. However, because of similarity in color between the stain and the stone's natural color, the specimens were exposed to the vapor for 5 days in a closed chamber in order to produce a darker stain. Treated weathered and unweathered specimens were sawed in half and exposed to the vapor for 5 days. This test was conducted after all previously mentioned tests were completed, or approximately two months after the two week curing period.

Both treated weathered and unweathered specimens showed consistent staining of equal intensity along the cross section. This would indicate that the treatment had fully penetrated and coated the entire 5x5x5 cm cube, and that the weathering process had not dissolved enough of the consolidant to markedly diminish the intensity of the stain. However, because of the length of time during which stones were exposed to the vapor, and chromatic similarity between the stones and the stain, results may not be as reliable as when conducted on lighter colored stones.

[31] Rakesh Kumar and William Ginell. "A New Technique for Determining the Depth of Penetration of Consolidants Into Limestone Using Iodine Vapor" in *Journal of the American Institute for Conservation, Vol. 36, #2.* (Washington: American Institute for Conservation of Historic and Artistic Works, 1997) pp. 17-21.

### 6.2.2 MICROSCOPY

Petrographic analyses of unweathered and weathered treated samples show that the consolidant could have reacted chemically with the stone. The crystalline band observed in the pores of untreated, unweathered samples (Fig. 34) significantly increased with consolidation (Fig. 35). This band diminished after weathering: in treated samples, the band was still strongly pronounced (Fig. 36), while in untreated samples, it was no longer observed.

After weathering, porosity in treated samples increased more than in untreated ones. The increased porosity in treated stones is observed in both matrix and rock fragments, although it is much more pronounced in the latter, suggesting the consolidant caused the preferential weathering of the more glassy rock fragments (Figs. 37 to 39).

Surfaces of treated, weathered samples showed similar but less severe alteration patterns than in untreated, weathered samples. Incidences of erosion around pumice and basalt clasts, increased porosity, and microcracking were diminished, although not altogether prevented by the treatment. White, crystalline efflorescences also formed on treated samples after weathering, which were visually different from those that formed on untreated, weathered samples.

In unweathered samples, the consolidant appears to have evenly coated the porous surface of the tuff (Fig. 40). The microcracking observed was most likely due to shrinkage during the drying process. However, the cracks appear isolated and unrelated to one another. (Fig. 41).

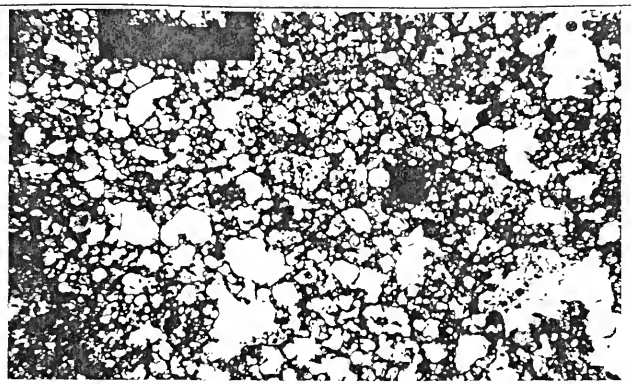


Fig. 37. Pumice clast in untreated, weathered sample

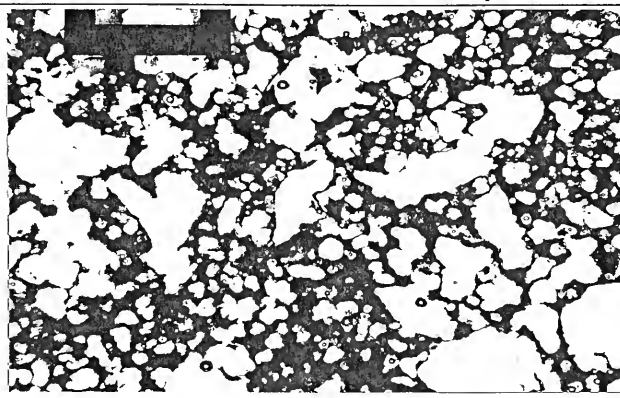


Fig. 38.Porosity of clast increases in treated, unweathered sample

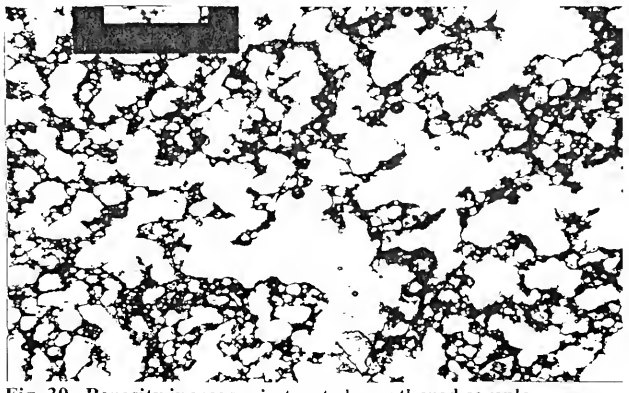


Fig. 39. Porosity increases in treated, weathered sample

**Figs. 37 to 39. Polarized light micrographs. Uncrossed polars, x 25.**

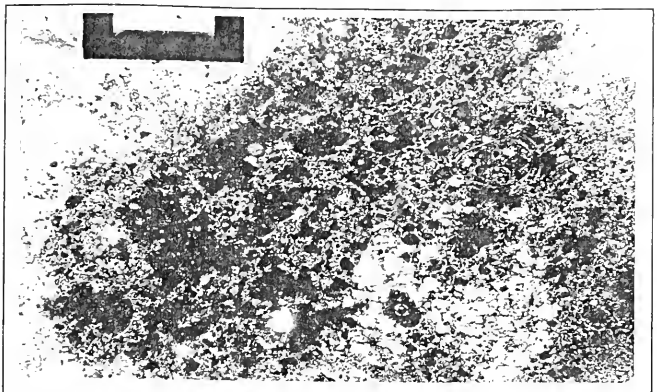


Fig. 34. Band is minimal in untreated, unweathered sample

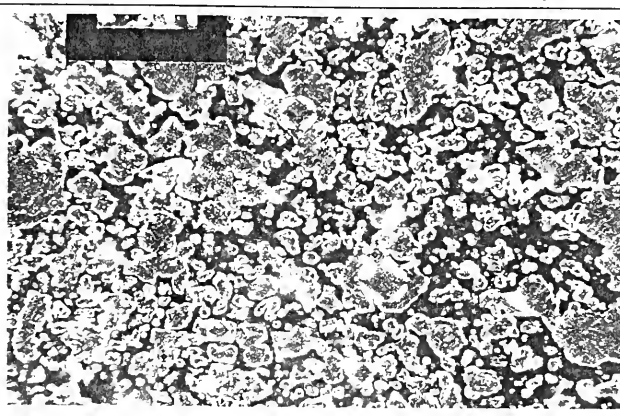


Fig. 35. Band is most pronounced in treated, unweathered sample

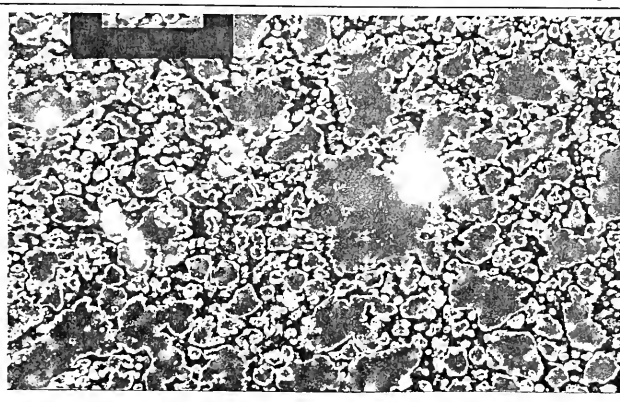


Fig. 36. This band diminishes in the treated, weathered sample

Figs.34 to 36. Polarized light micrographs. Uncrossed polars, x 25.

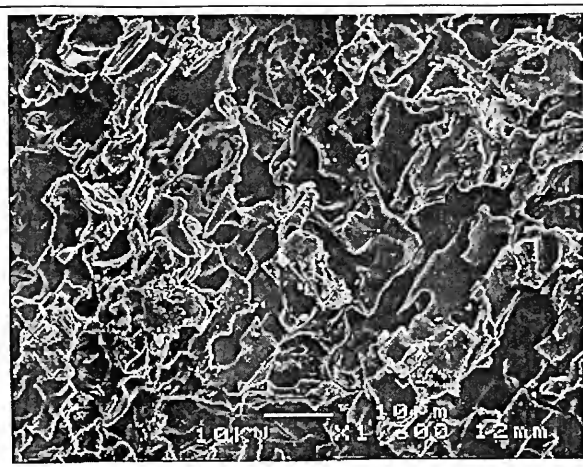



**Fig. 40 Evenly consolidated pumice clast SEM micrograph, x 1,300**

Weathering markedly increased the number of microcracks. The nature of cracking is unlike those found in the unweathered samples; cracks are interconnected and are generated from single points. (Fig. 42) There was no pattern established between the origin of the cracks within the sample, although a probable location is the boundary between matrix and clast. Conglomeration of cracks are a likely cause for preferential weakening and failure under much less loads than in unweathered samples.

In certain areas, the consolidant showed early signs of flaking. (Fig. 43) Flaked surfaces and microcracks are potential entry points between water and stone.

**Figure 41** Cracking of consolidant in unweathered Specimen.
SEM micrograph, X 1,000

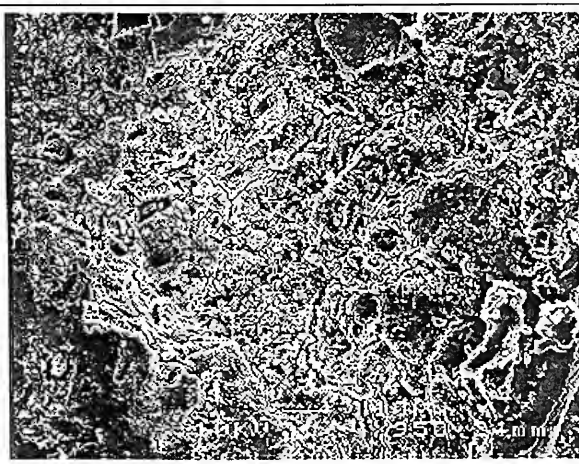


**Figure 42** Multiplicity of cracks generated from a single point in treated, weathered sample.
SEM micrograph, x 950

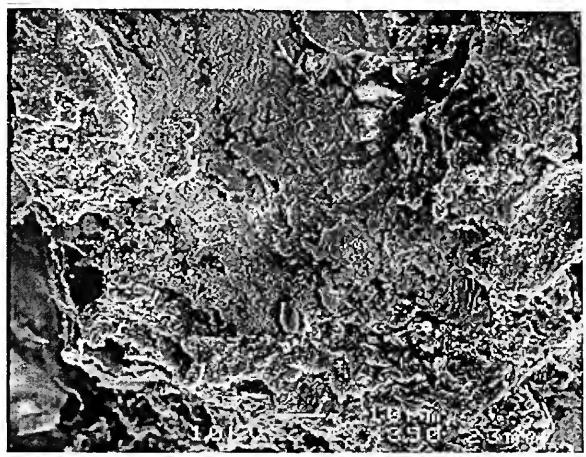


**Figure 43 Flaking of consolidant after weathering SEM micrograph, x 850**

### 6.2.3 CONDUCTIVITY AND pH

| Solution | pH | Conductance (μs) |
|---|---|---|
| Distilled Water | 4.65 | 0 |
| Water from Untreated Specimens | 6.9 | 190 |
| Water from Treated Specimens | 6.5 | 170 |
| Conservare OH Treatment (solution) | 5.0 | |

**Table 6. pH and Conductivity of the water in which stones were weathered**

The leaching of dissolved material from the stone is evidenced by the increase in conductivity of the water in which the stones were weathered, from 0μs (de-ionized water) to 170μs, as well as the increase in pH from 4.65 to 6.53. These values are similar to the conductance and pH of the water from untreated stones, and thus it is difficult to discern by this test alone whether it is the stone or the consolidant which had

dissolved. Furthermore, the pH of dissolved consolidant is expected to fall within the same range as the untreated stone because the polymerized consolidant is chemically akin to a silica gel.

### 6.2.4 COLOR

**Figure 44 Chromatic variations among**

1. **Unreated, Unweathered**
2. **Untreated, Weathered**
3. **Treated, Unweathered**
4. **Treated, Weathered**

The consolidant noticeably darkened the stone, (Fig. 44) but the discrepancy in colors evened out tone after completion of the weathering cycle. The color resulting from weathering is very similar to that of untreated weathered specimens. Chromatic alteration ranged from Munsell 10 YR 4/1 (untreated, unweathered) to Munsell 10 YR 3/1 (treated, unweathered) and back to its original color, 10YR 4/1.

### 6.3 POROSITY:

| Property | Treated Unweathered | | | | Treated, Weathered | | Difference | | |
|---|---|---|---|---|---|---|---|---|---|
| | D | E | F | G | F | G | F | G | % |
| Dry Weight | 211.2 | 206.4 | 216.2 | 191.45 | 207.29 | 184.47 | -8.91 | -6.98 | -3.90% |
| Saturated Wt. By Capillary Absorption | 248.03 | 240.42 | | | 253.86 | 226.4 | | | 12.46% |
| Saturated Weight by Total Immersion | 250.03 | 242.94 | | | 255.11 | 228.14 | | | 10.69% |
| Difference in absorbed water by 2 methods | 2 | 2.52 | | | 1.25 | 1.74 | | | -33.85% |
| % Porosity (using total immersion) | 18.39% | 17.70% | | | 23.07% | 23.67% | | | 5.33% |
| Capillary coefficient | 0.0019 | 0.0018 | | | 0.004 | 0.003 | | | |
| % Weight of Consolidant to Untreated Weight | 15% | 15.6% | 15.8% | 16% | 11% | 11.7% | | | |

**Table 7. Results of capillary absorption and total immersion for treated stones**

Average weight gain from the treatment is 27.7 g. After weathering, treated stones lost an average of 8 grams each, or approximately 28% of consolidant weight, and 3.9% of total weight (Table 7). Although certain parts of the stone dissolved as a result of weathering, most of the weight loss can be attributed to the dissolution of the consolidant, for the loss exceeds the 0.60 gram or 0.34% average weight loss in untreated stones by over ten times. Since both sets were weathered for the same amount of time, it is unlikely that the stone would have increased solubility ten times. That more of the consolidant and less of the stone dissolved would explain the visual difference between surface deposits of weathered, treated and untreated stones.

A 28% weight loss seemed an inordinate quantity to lose by such a short period of exposure to wet-dry cycles, and it was suggested by the lab manager of ProSoCo Inc. that this may be due to insufficient polymerization of the consolidant at the time of testing. Specimens are tested at the ProSoCo, Inc. laboratory after a three week minimum curing period per three cycles, which is the duration specified in the current product data sheets 1998-99.[32] This is a week longer than the curing time specified in data sheets printed in 1996, which was the schedule used for the study. Inadequate polymerization may partly explain this high value of consolidant loss.

In principle, the dissolution rate of the treated stone should have been much less than that of the untreated stone. However, the inordinate weight loss, conductivity and pH measurements almost equaling that of untreated stone attest to the instability of the polymerized product, even though the shorter curing time could partly account for it. These points shall be expounded on in the following sections.

| Property | Untreated | | Treated | |
|---|---|---|---|---|
| | Unweathered | Weathered | Unweathered | Weathered |
| Porosity | 32.3% | 34.2% | 18.1% | 23.4% |
| Capillary coefficient | 0.029 | 0.017 | 0.0018 | 0.004 |
| Difference in absorbed water by capillary Absorption & total immersion | 1.19 g. | 2.51 | 2.25 | 1.50 |

**Table 8. Averages for porosity and capillary coefficient for all stones**

A comparison of porosity percentages between unweathered, untreated (32.3%) and treated (18.1%) samples shows that Conservare OH Stone Strengthener significantly decreased porosity. Even after weathering, porosity of treated samples (23.4%), is still much lower than that of untreated, unweathered samples Table 8). However, despite the favorable effects on porosity, porosity increased by 5 percentage points after only 42 wet-dry cycles. Although this decrease may be partly due to the insufficient curing period, it does reflect the inherent properties of the polymerized consolidant. This makes treatment's long term durability and practicality in the field questionable.

### 6.3.1 Capillary Absorption

The capillary absorption rates of untreated stones were consistently uniform despite the heterogeneous nature of samples. The treatment produced a wider range of absorption rates but caused a significant reduction in the capillary absorption in unweathered samples from an average of 0.029 ($g./cm^3$)/hrs. (untreated) to 0.0018 ($g./cm^3$)/hrs. (treated). This rate increased slightly due to weathering, (0.0018 to 0.004 ($g./cm^3$)/hrs. but is still a substantial improvement over the rate of untreated specimens (Fig.45 & Table 9. For values derived for the chart, see Appendix II).

[32] Jennifer Moore, Laboratory Manager, ProSoCo, Inc. *Personal Interview.* May 16, 1999.

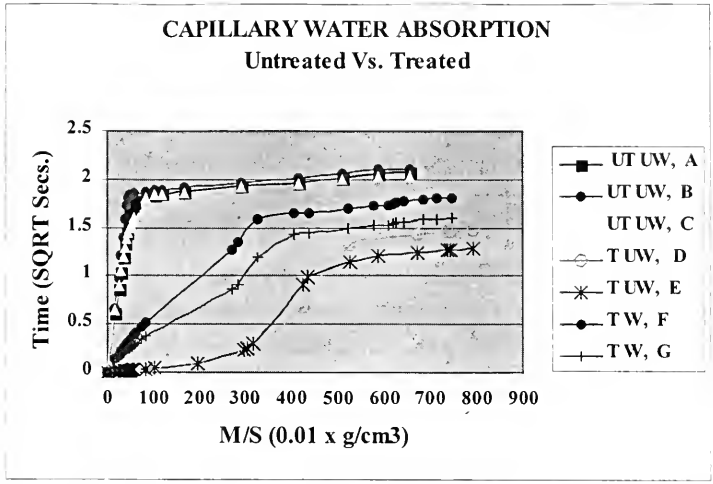



**Fig. 45 Capillary absorption chart for: Untreated, unweathered (UT, UW)**
**Treated, unweathered (T,UW)**
**Treated, Weathered (T,W)**

| Samples | Capillary Coefficient ( Ave. ((g./cm$^3$)/Time) |
|---|---|
| Unweathered, Untreated | 0.029 |
| Weathered, Untreated | 0.02 |
| Treated, Unweathered | 0.0018 |
| Treated, Weathered | 0.004 |

**Table 9. Capillary absorption coefficient**

Weathering produced contrasting capillary absorption rates between untreated and treated specimens. In the untreated set, the rate decreased, while it increased for the treated set. Thus weathering decreased pore size in untreated samples, while it increased pore size in treated samples. This suggests that the capillary absorption test was conducted during the initial stage of the stone's dissolution, which causes an increase in pore size. The second stage, pore shrinkage, caused by the deposition of dissolved minerals into interstices and pores, would probably occur after more than the 40

weathering cycles for it was not observed to transpire within the time frame of the experiment. Thus unlike the amorphous silica liberated from the untreated stone, the dissolved consolidant did not redeposit in large enough quantities to decrease pore size, although the amount was sufficient to precipitate on the surface.

### 6.3.2 TOTAL IMMERSION

After specimens reached constant weight (a weight difference not exceeding 0.01% between successive 24 hour weighings) by capillary absorption, these were immersed in water and again weighed until constant weight was reached. Results show that the difference in saturated weights between the two methods supports the hypothesis of increased pore size.

In treated samples, the weight increase from capillary absorption to total immersion averages 2.25 g. prior to weathering and only 1.5 g. after weathering. This signifies an increased porosity after weathering. In unweathered stones, a lower rate of absorption resulted in a lower quantity of water was absorbed by capillary action so that the incremental amount absorbed through total immersion was higher. Conversely, the higher absorption rate in weathered stones (caused by an increase in pore size) caused a higher quantity of water to be absorbed through capillary action, so that the incremental amount absorbed through total immersion was less. The opposite is true for untreated samples, which experienced a decrease in pore size after weathering.

### 6.3.3 Drying Behavior

The drying rate is lowest for treated, unweathered samples. The rate for the treated sample increases after weathering, presumably because of the increase in porosity and pore size. (Fig. 46. See Appendix III for values from which chart was derived.)

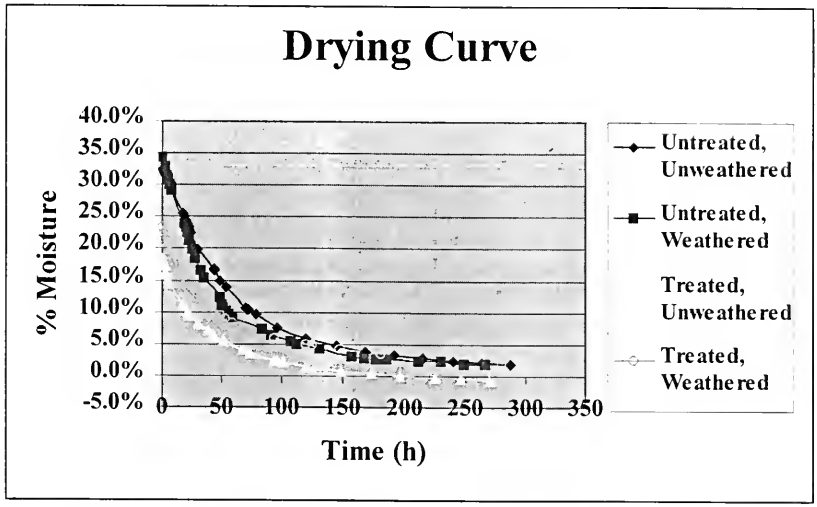



**Fig. 46 Drying Curve, Treated vs. Untreated samples**

| Drying Rate Coefficients for all Sample Sets (% Moisture Lost (g.)/ Time (h)) | |
|---|---|
| Untreated, Unweathered | Untreated, Weathered |
| -0.0042<br>-0.0039<br>-0.0041 | -0.0055<br>-0.0051<br>-0.0052 |
| Treated, Unweathered | Treated, Weathered |
| -0.0037<br>-0.0036 | -0.0045<br>-0.0048 |

**Table 10 Drying Rate Coefficients for all sample set**

## 6.4 MECHANICAL TESTS : COMPRESSIVE STRENGTH AND THREE-POINT BENDING TESTS

### 6.4.1 COMPRESSIVE STRENGTH

The Conservare OH Stone Strengthener treatment improved the stone's load bearing strength by 45%, from an average of 1,200 psi in untreated, unweathered samples, to 1,750 psi in treated, unweathered samples. The strength slightly decreased after weathering to 1,580, but is still higher than the original strength of the untreated, unweathered stone (Table 11).

That treated, unweathered samples took the same amount of time to reach their plastic limit at increased loads than untreated samples indicates embrittling, and is evidenced in the graphs by lower slopes. The brittleness of treated samples decreases after weathering, and the elasticity level reverts approximately to that of its untreated, unweathered state.

Weathering not only increases pliancy in the treated samples, but as shown by irregular dips along the slope, it also mechanically weakens these along certain areas and causes slight failure as the load progresses. This suggests that failure was caused by the large increases in porosity of the clasts compounded with the sudden formation of large microcracks elsewhere. In contrast, both untreated and treated unweathered samples exhibited more constant slopes, suggesting that elastic deformation was due to smaller microcracks that went undetected in the recording of failure (Fig. 42). The microcracking is likely due to the preferential weathering of the treated stone, as observed in the increased porosity of pumice and scoria clasts, and may be compounded with unevenly distributed consolidant.

This phenomena of larger microcracking is also observed in untreated, weathered samples. Thus while the consolidant does little to protect from small-scale preferential weakening, it does improve overall load-bearing capacity.

| Untreated Unweathered | Time (Minutes) | Load (Psi) |
|---|---|---|
| A | 57 secs. | 1,250 |
| B | 1 min. | 1,400 |
| C | 33 Secs | 1,050 |
| Untreated Weathered | | |
| A | 1 min. | 1,200 |
| B | 1 min. | 1,550 |
| C | 1.30 min. | 1,100 |
| Treated Unweathered | | |
| A | 50 Sec | 1,850 |
| B | 1 min. | 2,150 |
| C | 1.05 min. | 1,250 |
| Treated Weathered | | |
| A | 1.10 min | 1,550 |
| B | 1.30 min. | 1,550 |
| C | 50 secs | 1,650 |

**Table 11. Results of Compressive Strength tests**

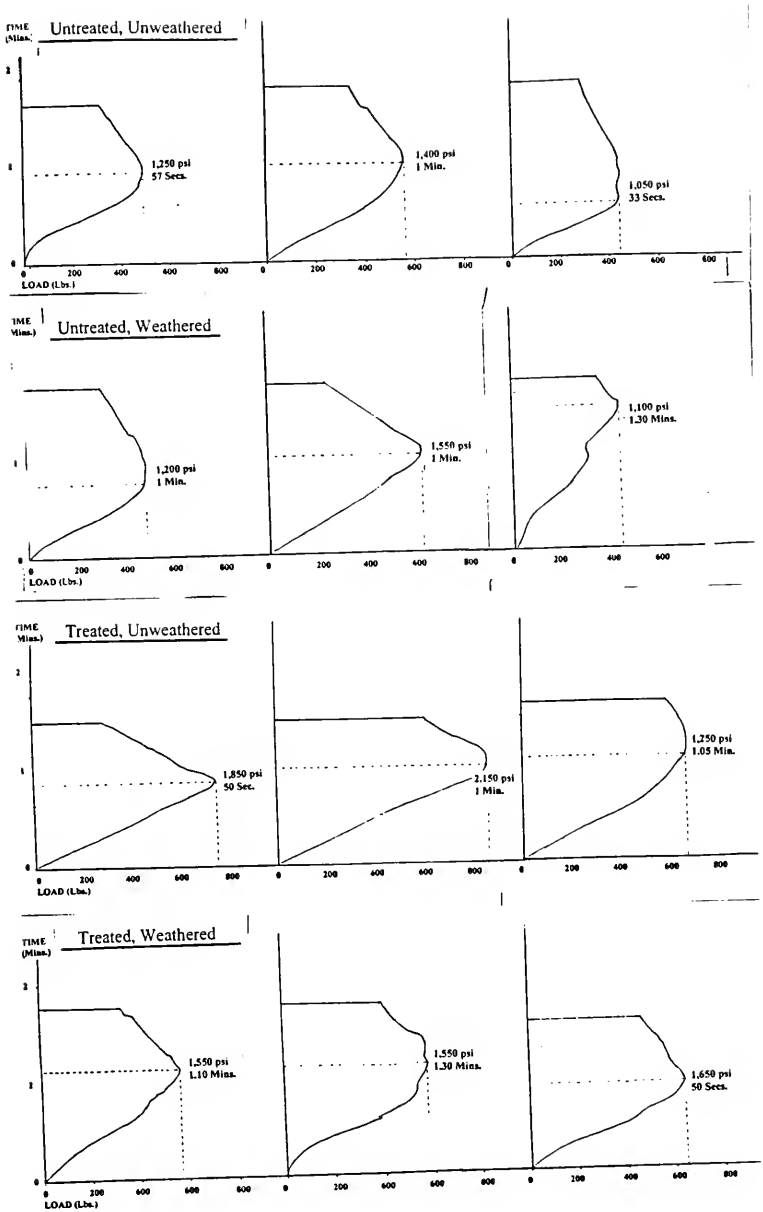



**Fig. 47. Chart for Compressive Strength test**

### 6.4.2 THREE POINT BENDING

The consolidant increased the bending strength from an average of 534 psi in untreated, unweathered samples to 743 psi in treated, unweathered samples, approximately a 40% increase. Weathering only slightly dropped this average to 703, which is still a 30% increase from the strength in untreated, unweathered samples. In conjunction with increased strength, the consolidant also imparted brittleness, which is indicated by a lower average displacement figure relative to load.

| Untreated Unweathered | Displacement (Inch) | Load (Lb.) |
|---|---|---|
| 1 | 0.0045 | 421 |
| 2 | 0.0062 | 606 |
| 3 | 0.0062 | 536 |
| 4 | 0.0065 | 573 |
| Untreated Weathered | | |
| 1 | 0.0045 | 592 |
| 2 | 0.0037 | 139 |
| 3 | 0.0057 | 398 |
| 4 | 0.0037 | 555 |
| Treated Unweathered | | |
| 1 | 0.006 | 772 |
| 2 | 0.0047 | 726 |
| 3 | 0.0052 | 698 |
| 4 | 0.0045 | 777 |
| Treated Weathered | | |
| 1 | 0.0072 | 563 |
| 2 | 0.0057 | 617 |
| 3 | 0.0060 | 719 |
| 4 | 0.0080 | 915 |

**Table 12. Results of 3-Point Bending tests**

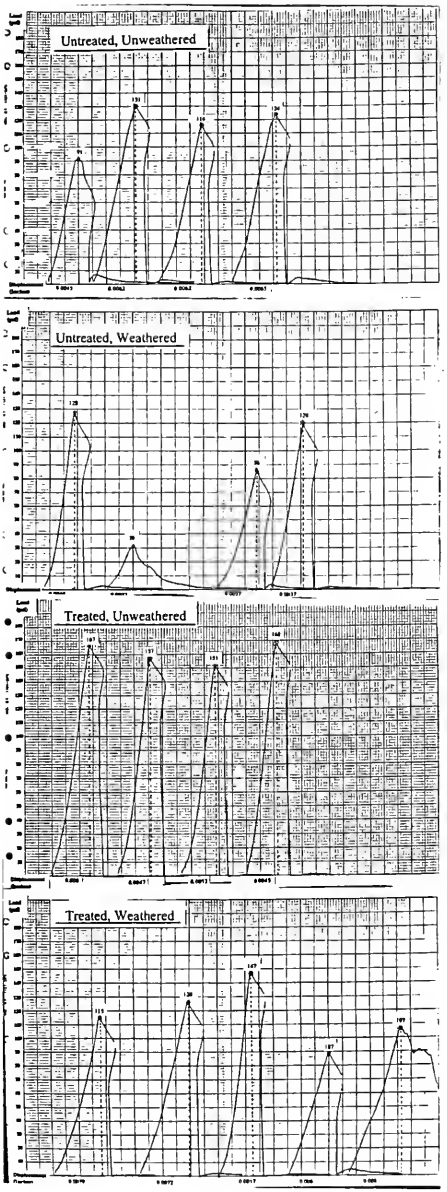



**Fig. 48 Charts for 3-Point Bending Test**

Weathering increased elasticity in both the treated and untreated sets, indicated by shifts in average displacement figures relative to the load (Fig. 48). Weathering also produced a more widely varied range of load limits: those for treated, unweathered samples is more consistent, with only a 79 lb. difference. In contrast, treated, weathered samples showed a more highly inconsistent range, differing by as much as 352 lbs. Again, this supports the hypothesis that preferential weathering weakened certain areas. The large variation may have been compounded with an unevenly distributed consolidant in the stone.

The stone's inherent heterogeneous nature causes a natural propensity for weak spots. This weakness is compensated for by the consolidant, which homogeneously coats and strengthens the stone, as indicated by more consistent displacement and load limit figures in treated, unweathered samples. However, weathering of the treated stones further magnifies this weakness by dissolving the consolidant and causing a greater concentration of stress on the weakened areas.

## 6.5 Discussion and Conclusion

The performance of a consolidant is highly influenced by the method of application, and conditions under which it is able to polymerize. If factors are not conducive to the formation of strong bonds, both to the stone and within the polymer itself, then the optimal properties of the treatment are not maximized. Factors such as high temperature and strong winds, a short curing time, an excess or deficiency of relative humidity leads to inadequate polymerization in the stone. All the above could have influenced the consolidation process.

Of these factors, short curing time and excessive moisture during curing are most likely to have partially influenced the performance of the treatment. A short curing period signifies that less of the pre-polymer had hydrolyzed and condensed, and thus could more easily have been lost during weathering. Also, when treated stones were exposed to water and moisture during weathering, hydrolysis was accelerated. As found by Charola, Wheeler, and Freund (1994), exposure to 100% RH will produce a better hydrolyzed polymer with only partial condensation. This results in a more elastic consolidant, albeit with increased stress microcracking (See fig. 38), which are both consistent with the mechanical test results for treated, weathered stones.

It must be noted that shorter curing time and exposure to weathering prior to the specified curing period is close a simulation to actual use on site, where curing time cannot be controlled in a laboratory environment, and the treated stones cannot be fully protected against the nuances of the weather.

Such favorable results as decreased porosity and capillary absorption and an improved mechanical strength show that the consolidant did impart some protection to the stone, although changes that resulted during the artificial weathering appear to indicate that this treatment is unlikely to withstand prolonged weathering in the field.

It is possible that the consolidant did react with the stone, based on the crystalline banding around pores which appeared to be most pronounced after treatment. The consolidant also fared poorly when weathered by water, even taking into account the shortened curing time. The test results that most supports the latter conclusion are excessive weight loss and inhomogeneous weathering. The inordinate quantity of leached product signifies its premature loss in certain areas of the stone, making these

especially susceptible to weathering. This conclusion is further supported by the increased porosity in clasts of treated, weathered stones over untreated, weathered stones.

Although treated stones exhibited the favorable property of increased elasticity when exposed to a highly humid environment, a property which enables stones to tolerate a larger range of stresses without permanent deformation, the above-mentioned weaknesses such as extensive stress microcracking suggest the treatment will provide only short-lived protection in the same environment. The treatment is thus better suited to drier climates.

# CHAPTER 7
# CONCLUSION

The Angono Petroglyph site is most threatened by flaking, spalling, and powdering of the stone, which occur mainly in areas displaying surface hardening and deposition of white crusts. These conditions proliferate closest to the areas with moisture filtrations, and thus continued activity of the mechanism promoting these conditions will most likely extend to the carvings themselves, ultimately resulting in their loss. Other mechanisms such as biological growth and animal infestation appear to pose a less localized threat, although they no doubt compound the overall problem of deterioration.

While the mechanisms responsible for promoting the less threatening conditions are quite apparent, the causes for surface flaking, powdering and encrustation are less obvious. Based on previous studies of naturally weathered tuff showing similar conditions, a hypothesis postulating the source of the conditions observed in the petroglyh site was formed: percolating water dissolves the vitreous constituents of the stone, and the substances are introduced into the solution. As the water evaporates, the substances are deposited on the surface, and this process continues until external pores are blocked. With less open pores by which to evaporate, any soluble salts such as those found in the rising damp will deteriorate the area by spalling and flaking. As long as water percolates or rises through the stone, the process will continue, and may repeat itself after the thick, dense surface has spalled.

In effort to test this hypothesis, samples of deteriorated rock from the petroglyph site and artificially weathered freshly quarried rock of the same geological formation as

the former were compared. A link is made between the conditions in the Angono petroglyph site, the conditions formed in the freshly quarried tuff, and their agents of deterioration.

Artificial weathering showed that the action of water promotes dissolution of the glassy constituents of the stone, which results in an increased porosity, erosion and loss of cohesion in the cementing matrix and rock fragments, and decrease in mechanical strength (see Appendix I for table summary of test results). The drying rate also increases because of the developed higher porosity. The dissolved constituents are deposited in capillaries, which results in the shrinking of existing pores, and / or formation of new and finer pores. When the solution is precipitated to the surface, white amorphous silica deposits are formed.

Most of the above stages, observed as a result of artificial weathering, suitably explain the conditions found on the petroglyph site. That glassy constituents are dissolved is confirmed by the presence of amorphous silica deposition in both naturally and artificially weathered samples. This signifies that some amount of stone has eroded and left a weaker and more porous stone in its stead. Pore size is also likely to have diminished in size from the deposition of silica in capillaries. These are all conditions that are promoted by the action of water alone.

While the amorphous silica deposits visually differ between the naturally and artificially weathered specimens, it is likely that the latter white and loosely deposited substance will eventually be transformed and compacted into the hardened layer by multiple subsequent depositions. However, the possibility exists that the precipitate was transformed into the dense layer by another mechanism aided by the action of other

factors such as organic acids emitted by biological growth. Likewise, it cannot be concluded that the increased drying rate is a property that will continue because the depositions of amorphous silica accumulate in pores and instead serve to deter the rate of drying, as is found on site. Thus while it is likely that this amorphous silica deposition will ultimately progress to form a hardened layer such as is observed in the petroglyph site, and that drying rates will initially increase due to porosity and then progressively decrease due to deposition of precipitated compounds, extended artificial weathering time is needed to ascertain these phenomena.

The effectiveness and durability of the consolidant, Conservare OH, was also tested by weathering. Not only did the treatment show capability of reaction with the stone, but it also showed favorable short-term results. It was effective to the extent that it decreased porosity and drying rate, and mechanically strengthened the stone. Results show that, despite reduction of these properties by weathering, the weathered, treated stone still manifested significant improvement over the untreated stones. That porosity increased suggests that the consolidant had protected most of the stone from dissolution so that this had not yet advance to the stage of silica deposition in sufficient quantities to decrease pore size.

However, although the treatment improved the stone's salient properties in the short-term, test results suggested otherwise of the consolidant's long term performance. Excessive dissolution and weight loss of the treated stone and preferential erosion of the rock fragments after just 42 weathering cycles in 21 days implies that its protective capacity in a highly humid environment will be short-lived. This could be due partly to the shorter curing time and early exposure to weathering, which are the same conditions

likely to be encountered in the field. This further supports the conclusion Conservare OH is not a suitable consolidant for a site that encounters high exposure to water and humidity, such as the tropics.

This study has explained immediate alterations in chemical and physical properties of treated and untreated volcanic tuffs that have weathered in an environment with high temperature and relative humidity and is frequently exposed to water.

While a short period of artificial weathering has resulted in conditions that reflect the long term trend of deterioration, its brevity precludes a thorough and in-depth understanding of the effects of sustained weathering. Results of the weathering of consolidated stones also raises questions as to the treatment's applicability in such climates as the tropics. It is therefore recommended that these areas be explored by further testing of samples weathered artificially over a prolonged period of time.

## Summary of Results From Tests and Analyses

| PROPERTY | UNTREATED | | TREATED | |
|---|---|---|---|---|
| | Unweathered | Weathered | Unweathered | Weathered |
| | | | | |
| Porosity | 32.30% | 34.22% | 18% | 23.40% |
| Capillary Absorption Coefficient | 0.029 | 0.019 | 0.0018 | 0.004 |
| Maximum Water Absorption by Capillary Action (g.) | 57 | 58.8 | 35.4 | 44.2 |
| Maximum Water Absorption by Total Immersion (g.) | 58 | 61.3 | 37.7 | 45.7 |
| Drying Curve, Initial Slope | -0.004 | -0.0052 | -0.00365 | -0.00465 |
| Compressive Strength (psi) | 1233 | 1283 | 1750 | 1583 |
| *Elasticity*<br>*Strength* | Semi-elastic<br>Homogeneous | Inconclusive<br>heterogeneous | Brittle<br>Homogeneous | Elastic<br>heterogeneous |
| Bending Strength (psi) | 534 | 421 | 743 | 703 |
| *Elasticity*<br>*Strength* | Semi-elastic<br>Homogeneous | Elastic<br>heterogeneous | Brittle<br>Homogeneous | Semi-elastic<br>heterogeneous |
| Color | Yellow-brown | | Dark Yellow-brown | |
| | | Blue-gray | | Blue-Gray |
| Petrography | Fractured feldspars<br>Homogeneous in color | Semi-porous clasts<br>Widened fractures<br>Lightening/erosion | Porous clasts | Highly porous clasts |
| SEM | | | Even coat | Flaking |
| | | | Shrinkage cracks | Stress cracks |
| Formation of Surface Deposit | none | 1 of 3 samples | none | 2 of 2 samples |

Raw Data, Capillary Absorption

UNTREATED UNWEATHERED SPECIMENS

| TIME SQRT S | M/S (10 -2 g/cm2) A UW | B UW | C UW |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 17.3 | 0.61 | 0.66 | 0.64 |
| 24.5 | 0.86 | 0.98 | 0.89 |
| 30.0 | 1.03 | 1.21 | 1.05 |
| 34.6 | 1.19 | 1.41 | 1.19 |
| 38.7 | 1.33 | 1.58 | 1.29 |
| 42.4 | 1.45 | 1.73 | 1.38 |
| 45.8 | 1.56 | 1.81 | 1.45 |
| 49.0 | 1.65 | 1.84 | 1.49 |
| 52.0 | 1.71 | 1.84 | 1.52 |
| 54.8 | 1.74 | 1.85 | 1.55 |
| 57.4 | 1.76 | 1.85 | 1.58 |
| 60.0 | 1.77 | 1.85 | 1.61 |
| 84.9 | 1.83 | 1.87 | 1.80 |
| 103.9 | 1.84 | 1.88 | 1.83 |
| 120.0 | 1.85 | 1.89 | 1.84 |
| 169.7 | 1.87 | 1.91 | 1.86 |
| 293.9 | 1.93 | 1.97 | 1.91 |
| 415.7 | 1.97 | 2.02 | 1.95 |
| 509.1 | 2.01 | 2.07 | 2.00 |
| 587.9 | 2.06 | 2.10 | 2.02 |
| 657.3 | 2.07 | 2.11 | 2.02 |
| CAPILLARY COEFFICIENT | 0.02839 | 0.03878 | 0.01735 |

Raw Data, Capillary Absorption

UNTREATED, WEATHERED SPECIMENS

| TIME | M/S (10 -2 g/cm2) | | |
|---|---|---|---|
| SQRT S | AW | BW | CW |
| 0 | 0 | 0 | 0 |
| 17.32 | 0.46 | 0.53 | 0.46 |
| 24.49 | 0.61 | 0.71 | 0.55 |
| 30.00 | 0.75 | 0.88 | 0.63 |
| 34.64 | 0.87 | 1.02 | 0.70 |
| 38.73 | 0.97 | 1.13 | 0.75 |
| 42.43 | 1.06 | 1.23 | 0.80 |
| 45.83 | 1.14 | 1.32 | 0.85 |
| 48.99 | 1.22 | 1.40 | 0.89 |
| 57.45 | 1.43 | 1.60 | 1.01 |
| 64.81 | 1.62 | 1.72 | 1.13 |
| 84.85 | 1.77 | 1.83 | 1.43 |
| 103.92 | 1.81 | 1.88 | 1.75 |
| 169.71 | 1.87 | 1.93 | 1.86 |
| 180.00 | 1.90 | 1.94 | 1.87 |
| 247.39 | 1.93 | 1.98 | 1.90 |
| 274.95 | 1.95 | 1.98 | 1.92 |
| 281.42 | 1.95 | 1.99 | 1.93 |
| 326.80 | 2.01 | 2.03 | 1.97 |
| 396.48 | 2.05 | 2.09 | 2.04 |
| 401.75 | 2.06 | 2.09 | 2.04 |
| 491.73 | 2.08 | 2.12 | 2.07 |
| 502.00 | 2.09 | 2.13 | 2.08 |
| 519.62 | 2.09 | 2.13 | 2.08 |
| 572.36 | 2.11 | 2.15 | 2.10 |
| 657.27 | 2.13 | 2.17 | 2.08 |
| 722.50 | 2.13 | 2.17 | 2.13 |
| Capillary Coefficient | 0.021 | 0.037 | 0.023 |

Raw Data, Capillary Absorption

TREATED, UNWEATHERED SPECIMENS

| TIME | M/S (10 -2 g/cm2) | |
|---|---|---|
| SQRT S | D | E |
| 0.00 | 0.000 | 0.000 |
| 17.32 | 0.013 | 0.010 |
| 24.49 | 0.016 | 0.012 |
| 30.00 | 0.017 | 0.016 |
| 34.64 | 0.020 | 0.017 |
| 38.73 | 0.021 | 0.018 |
| 42.43 | 0.021 | 0.019 |
| 45.83 | 0.023 | 0.021 |
| 48.99 | 0.025 | 0.023 |
| 51.96 | 0.027 | 0.023 |
| 54.77 | 0.028 | 0.025 |
| 57.45 | 0.030 | 0.027 |
| 60.00 | 0.030 | 0.026 |
| 84.85 | 0.043 | 0.038 |
| 103.92 | 0.051 | 0.045 |
| 199.00 | 0.099 | 0.089 |
| 300.00 | 0.224 | 0.235 |
| 305.94 | 0.238 | 0.258 |
| 317.49 | 0.253 | 0.296 |
| 424.26 | 0.676 | 0.913 |
| 436.81 | 0.816 | 0.984 |
| 526.50 | 1.321 | 1.149 |
| 587.88 | 1.389 | 1.213 |
| 673.50 | 1.427 | 1.241 |
| 737.29 | 1.455 | 1.266 |
| 744.58 | 1.458 | 1.268 |
| 793.73 | 1.483 | 1.290 |
| Capillary Coefficient | 0.0019 | 0.0015 |

Raw Data, Capillary Absorption

TREATED, WEATHERED SPECIMENS

| TIME | M/S (10 -2 g/cm2) | |
|---|---|---|
| SQRT S | F | G |
| 0 | 0 | 0 |
| 17.32 | 0.136 | 0.126 |
| 24.49 | 0.174 | 0.153 |
| 30.00 | 0.218 | 0.182 |
| 34.64 | 0.247 | 0.202 |
| 38.73 | 0.271 | 0.217 |
| 42.43 | 0.291 | 0.233 |
| 45.83 | 0.311 | 0.245 |
| 48.99 | 0.327 | 0.255 |
| 51.96 | 0.344 | 0.265 |
| 54.77 | 0.358 | 0.275 |
| 57.45 | 0.375 | 0.284 |
| 60.00 | 0.393 | 0.295 |
| 62.45 | 0.408 | 0.303 |
| 75.50 | 0.472 | 0.345 |
| 84.85 | 0.525 | 0.380 |
| 271.66 | 1.271 | 0.860 |
| 284.60 | 1.351 | 0.909 |
| 328.63 | 1.584 | 1.188 |
| 406.94 | 1.646 | 1.436 |
| 438.86 | 1.658 | 1.452 |
| 522.49 | 1.692 | 1.489 |
| 577.58 | 1.723 | 1.522 |
| 609.43 | 1.732 | 1.532 |
| 619.68 | 1.752 | 1.547 |
| 626.90 | 1.759 | 1.555 |
| 643.89 | 1.770 | 1.563 |
| 684.54 | 1.799 | 1.585 |
| 715.40 | 1.807 | 1.593 |
| 747.40 | 1.812 | 1.597 |
| CAPILLARY COEFFICIENT | 0.0044 | 0.0032 |

Drying Curve, Raw Data

UNTREATED, UNWEATHERED

| Time Hrs. | % Absorbed | | |
|---|---|---|---|
| | A UW | B UW | C UW |
| 0 | 32.82% | 32.08% | 32.02% |
| 1 | 32.49% | 31.82% | 31.77% |
| 2 | 32.27% | 31.63% | 31.59% |
| 3 | 31.94% | 31.32% | 31.29% |
| 4 | 31.52% | 30.95% | 30.91% |
| 5 | 31.15% | 30.62% | 30.55% |
| 6 | 30.53% | 30.00% | 29.89% |
| 18 | 25.86% | 25.60% | 25.23% |
| 19 | 25.35% | 25.14% | 24.74% |
| 20 | 24.72% | 24.55% | 24.15% |
| 21 | 24.18% | 24.05% | 23.66% |
| 22 | 23.61% | 23.50% | 23.12% |
| 23 | 23.03% | 22.98% | 22.59% |
| 24 | 22.50% | 22.47% | 22.13% |
| 30 | 19.98% | 19.98% | 19.55% |
| 43 | 16.90% | 17.02% | 16.68% |
| 44 | 16.49% | 16.60% | 16.28% |
| 48 | 14.98% | 15.15% | 14.90% |
| 54 | 13.95% | 14.16% | 13.98% |
| 70 | 10.62% | 10.82% | 10.61% |
| 71 | 10.41% | 10.61% | 10.42% |
| 72 | 10.26% | 10.48% | 10.27% |
| 78 | 9.56% | 9.75% | 9.61% |
| 96 | 7.28% | 7.66% | 7.57% |
| 120 | 5.74% | 5.98% | 5.88% |
| 144 | 4.61% | 4.79% | 4.67% |
| 168 | 3.56% | 3.79% | 3.74% |
| 192 | 3.30% | 3.48% | 3.43% |
| 216 | 2.64% | 2.79% | 2.74% |
| 240 | 2.31% | 2.42% | 2.38% |
| 264 | 2.11% | 2.14% | 2.12% |
| 288 | 1.91% | 1.94% | 1.89% |

Drying Curve, Raw Data

UNTREATED, WEATHERED

| Time Hrs. | % Absorbed | | |
|---|---|---|---|
| | A W | B W | C W |
| 0 | 34.72% | 33.72% | 34.23% |
| 2 | 33.34% | 32.43% | 32.85% |
| 4 | 31.83% | 31.21% | 31.51% |
| 5 | 31.26% | 30.66% | 31.00% |
| 6 | 30.43% | 29.84% | 30.14% |
| 7 | 29.92% | 29.44% | 29.66% |
| 8 | 29.27% | 28.76% | 28.99% |
| 19 | 23.90% | 24.07% | 24.06% |
| 20 | 23.48% | 23.27% | 23.65% |
| 21 | 22.59% | 22.37% | 22.74% |
| 22 | 21.96% | 21.78% | 22.20% |
| 23 | 21.26% | 21.08% | 21.46% |
| 25 | 19.70% | 19.59% | 19.96% |
| 27 | 18.40% | 18.41% | 18.71% |
| 33 | 16.44% | 16.58% | 16.82% |
| 35 | 15.23% | 15.42% | 15.65% |
| 48 | 12.03% | 12.28% | 12.29% |
| 50 | 11.47% | 11.69% | 9.96% |
| 51 | 11.15% | 11.37% | 9.64% |
| 53 | 10.69% | 10.94% | 9.18% |
| 56 | 10.21% | 10.49% | 8.71% |
| 59 | 9.50% | 9.79% | 8.01% |
| 84 | 7.61% | 7.85% | 6.15% |
| 91 | 6.72% | 6.98% | 5.27% |
| 107 | 5.93% | 6.16% | 4.49% |
| 112 | 5.40% | 5.64% | 3.97% |
| 131 | 4.56% | 4.81% | 3.14% |
| 157 | 3.38% | 3.69% | 1.97% |
| 167 | 3.31% | 3.57% | 1.90% |
| 177 | 3.03% | 3.22% | 1.62% |
| 186 | 2.92% | 3.14% | 1.52% |
| 212 | 2.77% | 2.95% | 1.37% |
| 230 | 2.70% | 2.85% | 1.30% |
| 249 | 2.37% | 2.47% | 0.97% |
| 266 | 2.24% | 2.27% | 0.85% |

Drying Curve, Raw Data

TREATED, UNWEATHERED

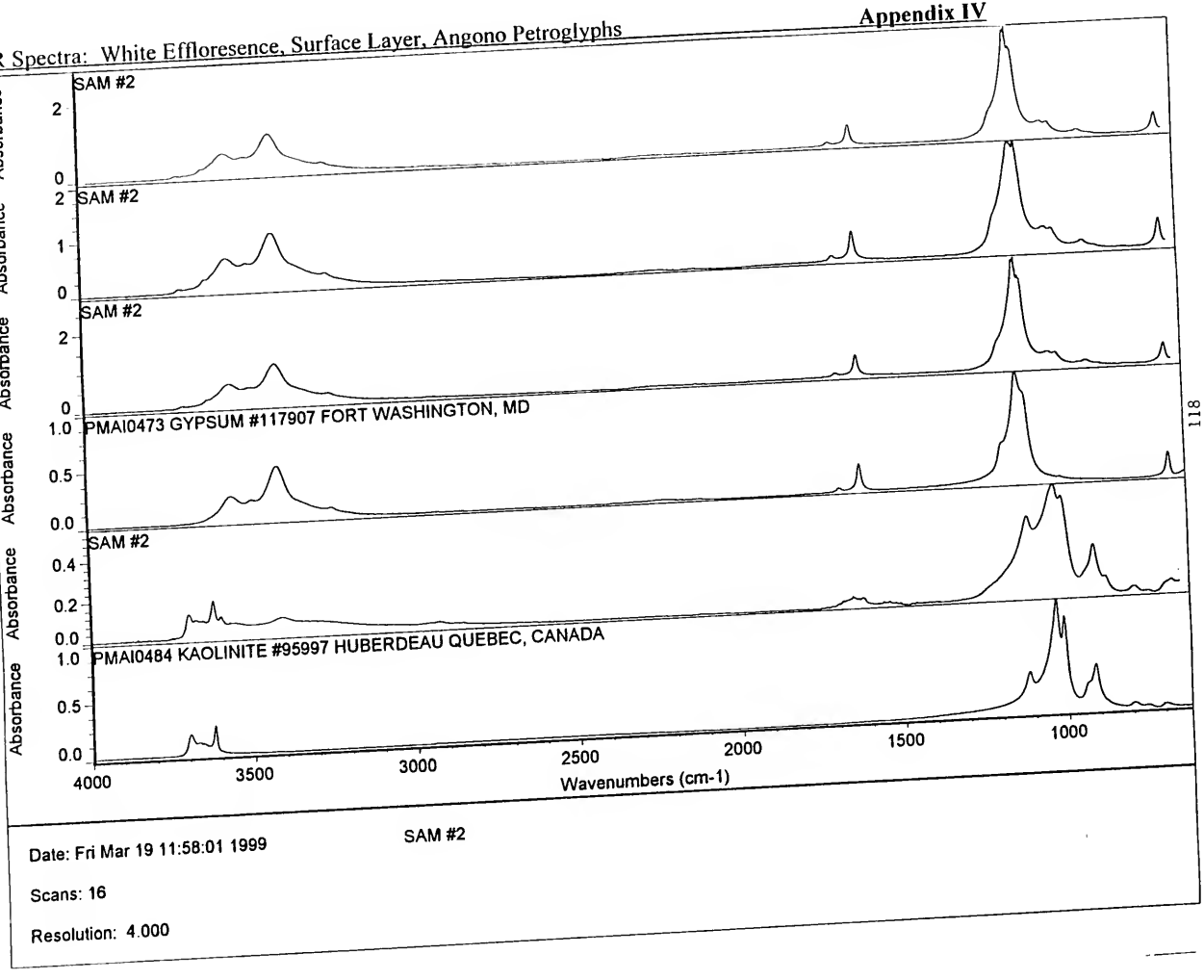
| Time Hrs. | % Absorbed | |
|---|---|---|
| | D UW | E UW |
| 0 | 18.59% | 18.17% |
| 1 | 18.02% | 17.57% |
| 2 | 17.44% | 16.95% |
| 3 | 16.56% | 16.08% |
| 4 | 16.02% | 15.57% |
| 5 | 15.36% | 14.91% |
| 6 | 14.60% | 14.15% |
| 18 | 11.29% | 10.99% |
| 21 | 10.14% | 9.83% |
| 22 | 9.87% | 9.57% |
| 23 | 9.67% | 9.38% |
| 30 | 8.47% | 8.23% |
| 31 | 8.25% | 7.99% |
| 39 | 7.12% | 6.84% |
| 42 | 6.54% | 6.24% |
| 44 | 6.28% | 6.02% |
| 51 | 5.55% | 5.31% |
| 67 | 4.00% | 3.77% |
| 73 | 3.63% | 3.37% |
| 93 | 2.47% | 2.25% |
| 96 | 2.35% | 2.15% |
| 101 | 2.15% | 1.97% |
| 120 | 1.42% | 1.19% |
| 148 | 0.67% | 0.49% |
| 173 | 0.44% | 0.29% |
| 197 | 0.09% | -0.08% |
| 225 | -0.23% | -0.36% |
| 246 | -0.53% | -0.67% |
| 270 | -0.70% | -0.78% |

Drying Curve, Raw Data

TREATED, WEATHERED

| Time | % Absorbed | |
|---|---|---|
| Hrs. | F W | F W |
| 0 | 23.07% | 23.67% |
| 1 | 22.01% | 22.58% |
| 2 | 21.32% | 21.79% |
| 4 | 20.13% | 20.46% |
| 6 | 19.21% | 19.63% |
| 10 | 17.17% | 17.63% |
| 18 | 14.25% | 14.22% |
| 20 | 13.83% | 13.71% |
| 29 | 12.13% | 12.01% |
| 48 | 9.94% | 9.18% |
| 52 | 9.27% | 8.58% |
| 58 | 8.55% | 7.83% |
| 73 | 7.57% | 6.66% |
| 94 | 6.38% | 5.51% |
| 119 | 5.31% | 4.72% |
| 124 | 5.18% | 4.59% |
| 147 | 4.43% | 3.88% |
| 181 | 3.78% | 3.19% |
| 206 | 3.35% | 2.80% |
| 231 | 2.93% | 2.40% |
| 256 | 2.55% | 2.14% |
| 276 | 2.33% | 1.97% |
| 280 | 2.32% | 1.94% |

IR Spectra: White Effloresence, Surface Layer, Angono Petroglyphs

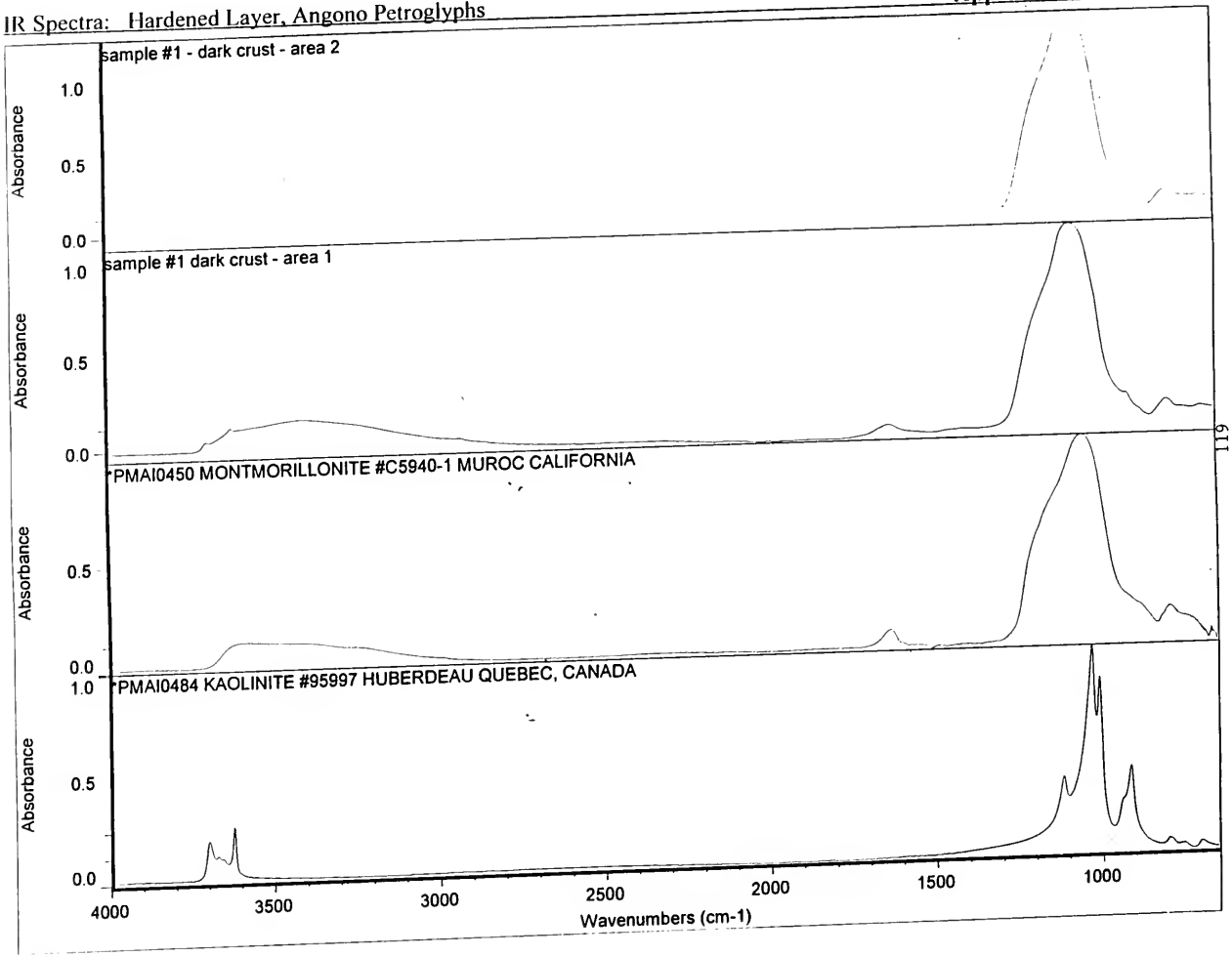



Date: Fri Mar 19 11:58:01 1999 SAM #2

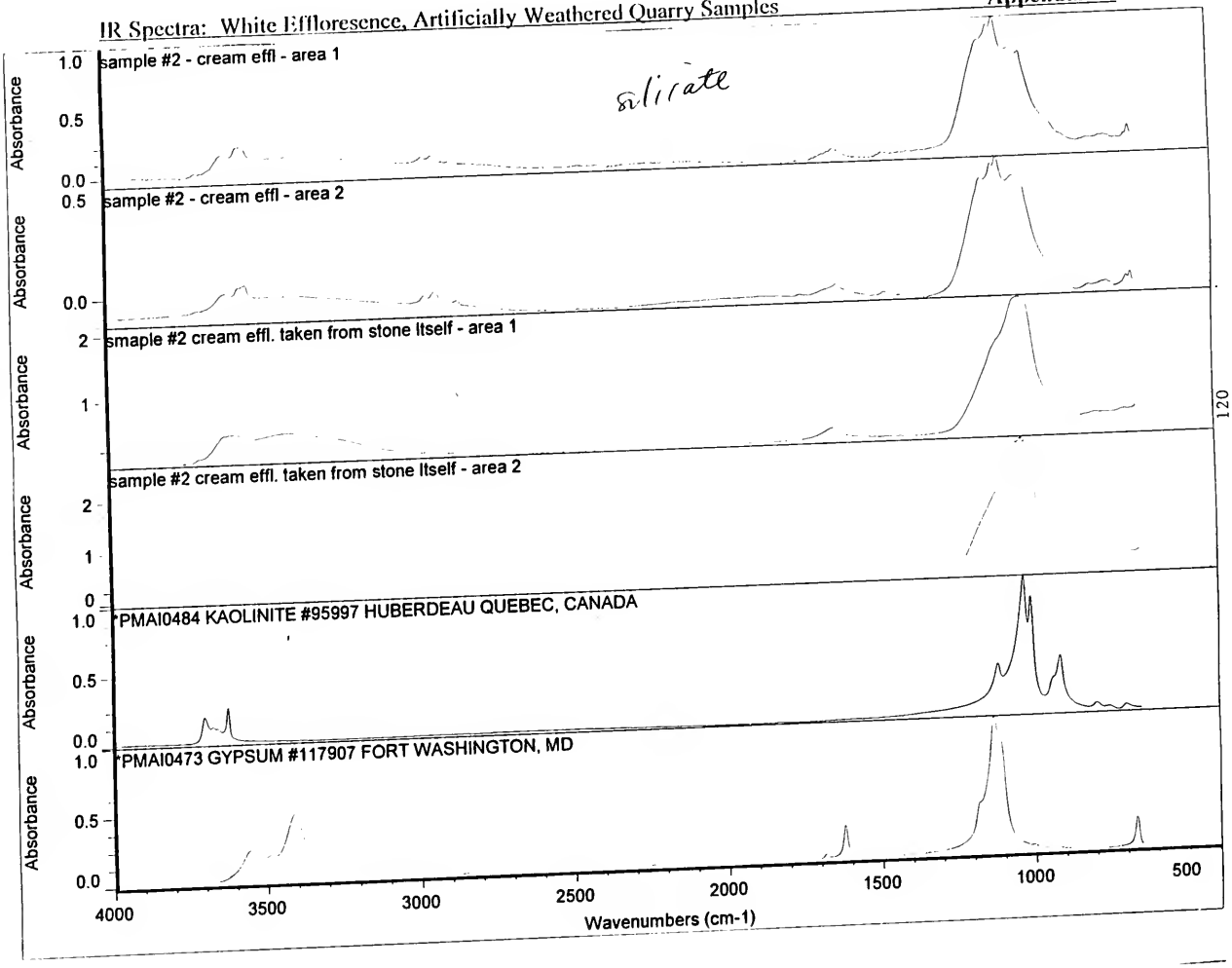
Scans: 16

Resolution: 4.000

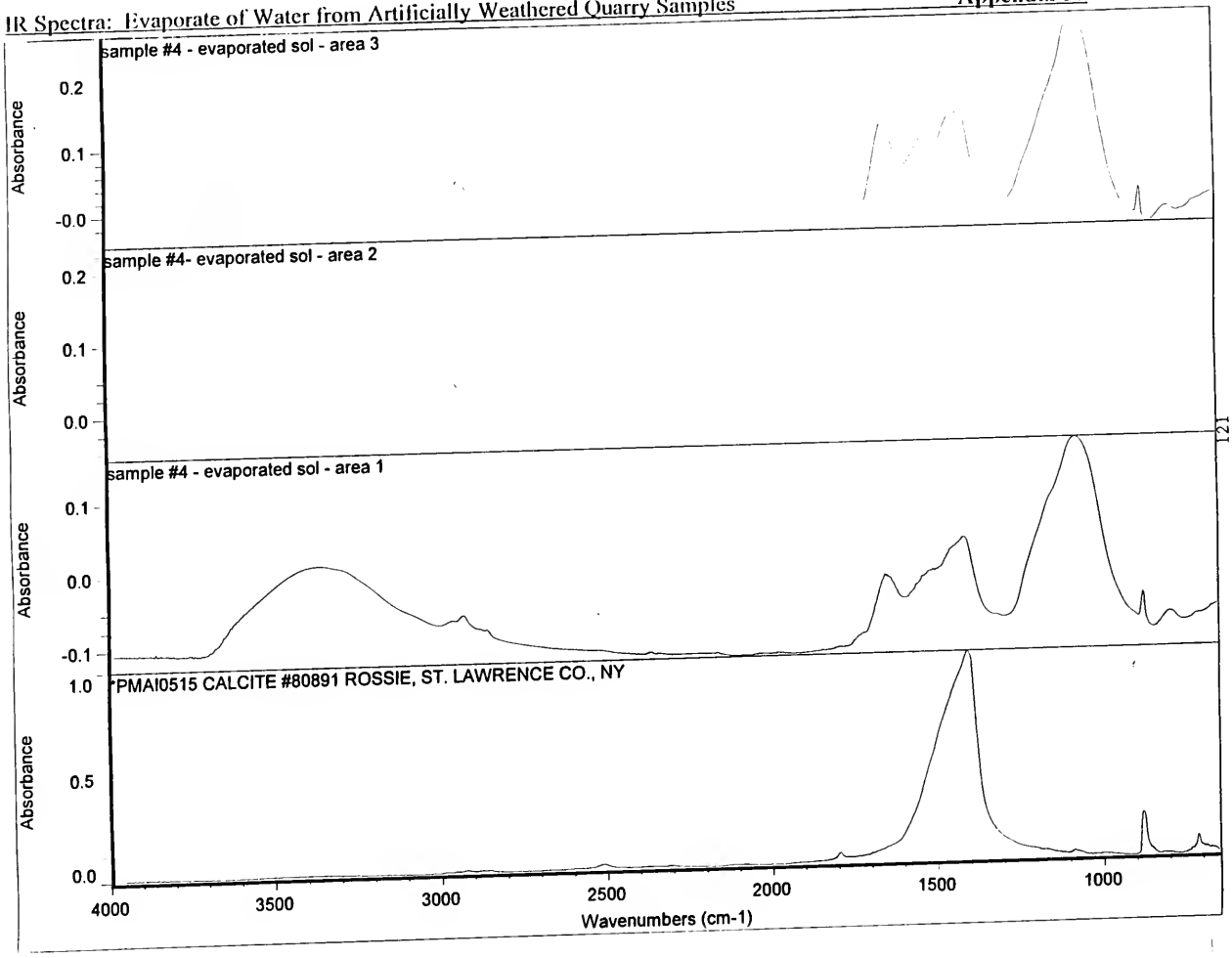
IR Spectra: Hardened Layer, Angono Petroglyphs



IR Spectra: White Efflorescence, Artificially Weathered Quarry Samples



IR Spectra: Evaporate of Water from Artificially Weathered Quarry Samples



Climatological Normals, Quezon City

CLIMATOLOGICAL NORMALS
STATION :430 - SCIENCE GARDEN, QUEZON CITY
LATITUDE :14°39' N
LONGITUDE :121°03' E
ELEVATION : 43.0 m
PERIOD :1961 - 1995

| MONTH | RAIN-FALL MM | NO OF RD | TEMPERATURE DEG. C MAX. | MIN. | MEAN | DRY BULB | WET BULB | DEW PT. | VP MBS. | RH % | MSLP MBS. | WIND DIR | SPD MPS | CLD OKT | DAYS TSTM | WITH LTNG |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| JAN. | 18.7 | 4 | 30.2 | 20.1 | 25.2 | 25.0 | 21.8 | 20.5 | 23.9 | 76 | 1012.5 | NE | 2 | 5 | 0 | 0 |
| FEB. | 7.4 | 2 | 31.4 | 20.2 | 25.8 | 25.7 | 21.7 | 20.0 | 23.2 | 70 | 1012.4 | NE | 2 | 4 | 0 | 0 |
| MAR. | 16.7 | 3 | 33.2 | 21.4 | 27.3 | 27.3 | 22.6 | 20.7 | 24.2 | 67 | 1011.8 | SE | 2 | 4 | 1 | 1 |
| APR. | 28.5 | 4 | 34.8 | 22.9 | 28.9 | 28.9 | 23.8 | 21.9 | 26.0 | 65 | 1010.3 | SE | 2 | 4 | 3 | 3 |
| MAY | 141.0 | 11 | 34.6 | 24.1 | 29.3 | 29.2 | 25.0 | 23.5 | 28.8 | 71 | 1008.6 | SE | 2 | 5 | 12 | 13 |
| JUNE | 344.6 | 18 | 32.5 | 24.0 | 28.3 | 28.0 | 25.2 | 24.2 | 30.1 | 80 | 1008.0 | SW | 2 | 6 | 16 | 16 |
| JULY | 478.6 | 22 | 31.3 | 23.6 | 27.5 | 27.1 | 24.9 | 24.1 | 30.0 | 84 | 1007.6 | SW | 2 | 6 | 17 | 13 |
| AUG. | 517.1 | 24 | 30.8 | 23.6 | 27.2 | 26.9 | 24.8 | 24.0 | 29.8 | 84 | 1006.5 | SW | 2 | 7 | 14 | 9 |
| SEPT | 402.2 | 22 | 31.1 | 23.4 | 27.3 | 26.8 | 24.8 | 24.1 | 29.9 | 85 | 1008.1 | SW | 2 | 7 | 15 | 12 |
| OCT. | 268.2 | 18 | 31.1 | 22.8 | 27.0 | 26.6 | 24.3 | 23.5 | 28.8 | 83 | 1009.0 | N | 2 | 6 | 10 | 8 |
| NOV. | 147.2 | 13 | 30.9 | 22.0 | 26.4 | 26.1 | 23.6 | 22.7 | 27.4 | 81 | 1010.3 | N | 2 | 5 | 4 | 3 |
| DEC. | 61.9 | 8 | 30.2 | 21.0 | 25.6 | 25.3 | 22.5 | 21.4 | 25.3 | 79 | 1011.7 | NE | 2 | 5 | 1 | 1 |
| ANNUAL | 2431.9 | 149 | 31.8 | 22.4 | 27.1 | 26.9 | 23.7 | 22.5 | 27.3 | 77 | 1009.8 | SW | 2 | 5 | 93 | 76 |

PREPARED BY: PAGASA/CAB/CDS

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